STUDIES OF AMPHIPHILIC SYSTEMS

ABSTRACT

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

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IN

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BY

DAKSHA SHARMA

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Abstract

Surfactant molecules are known to form supramolecular aggregates when they are dissolved in aqueous medium beyond a certain concentration known as critical micellar concentration (cmc). The last few decades of the 20th century have witnessed a rapid change in the field of research on surfactant systems and molecular aggregates.[1-7] This field has emerged as a major thrust area of interdisciplinary research comprising of colloids, micelles, emulsions, macromolecules, liquid crystals, membranes, nanoparticles, supramolecular aggregates, drug encapsulation, etc. The work produced in the field is not only of basic scientific interest, but is also relevant to a broad range of technologies (like detergency, lubrication, agricultural sprays, textiles, mineral floatation, microelectronics, food, petroleum, pharmaceutical, biotechnology, etc.). In fact, this research area has applications in everyday life and promising industrial growth and helps in understanding the intricacies of the life processes.

Micellization is primarily driven by the tendency of the hydrophobic moieties to reduce the hydrocarbon-water contact. This effect is counteracted by head group repulsion in ionic surfactants. The hydrocarbon chain, head group and counterions all play their part in this delicate balance of molecular interactions, which determines the size and shape of the aggregates. One of the most important features of micelles is their capacity to solubilize hydrophobic molecules in aqueous solution.

The work described in the thesis is devoted to studies on certain aspects of surfactants in solution (micellization, solubilization, morphology) in presence of salts and/or organic additives. The

additive induced changes are important as they may drastically improve and, in some cases, modify performance of surfactant based products and make them usable for specific purposes.

In the **General Introduction (Chapter – I)**, a detailed account of the behavior of surfactants and various phenomena exhibited by them, for example, micellization, causes of micellization, factors affecting cmc and micellar shape/size, thermodynamics of micellization, and the effect of additives are described. An up-to-date literature survey related to the work described in subsequent chapters is also included.

Chapter – II contains experimental details. The source and purity of various chemicals are mentioned in this chapter. This chapter also contains sample preparation, methodologies, and relevant theoretical aspects of different measurements performed on surfactant solutions.

Chapter-III deals with micellization of an anionic surfactant sodium dodecylbenzenesulfonate (SDBS) in the presence of inorganic and symmetrical quaternary salts. For the purpose the effect of addition of LiBr, NaBr, and NH_4Br on micellization parameters (i.e., cmc and degree of counterion dissociation, α) of SDBS has been studied using conductivity measurements at 25 °C. The effect of these inorganic salts is compared with those of symmetrical quaternary bromides, namely, tetramethylammonium bromide (Me_4NBr), tetraethylammonium bromide (Et_4NBr), tetra-*n*-propylammonium bromide (Pr_4NBr), tetra-*n*-butylammonium bromide (Bu_4NBr), tetra-*n*-butylphosphonium bromide (Bu_4PBr), and tetraphenylphosphonium bromide (ϕ_4PBr). As usual, the presence of salts bring about a reduction in cmc but salts containing bulky

counterions (symmetrical quaternary) show progressively increased effect both on cmc (Fig. 1) and α (Table 1). The bulky counterions seem to weaken hydration forces with concomitant decrease in cmc. The results are further interpreted in the light of hydrophobic interactions (among alkyl/phenyl chains of the respective salt and sufactant monomers of the micelle) in addition to the neutralization of surface charge due to salt addition. Connecting atom (N or P) in a quaternary salt seems to play an important role in such interactions as Bu_4PBr and ϕ_4PBr are more effective in decreasing the cmc. Therefore, the quaternary salts could be an ideal candidate to vary hydration forces in anionic micellar solutions.

The role of quaternary bromides in changing the solubilization site of organic additives in cationic micellar solutions has been studied and the results are included in **Chapter-IV**. Newtonian flow conditions were adopted to conduct viscosity measurements at 30 °C on solutions of two cationic surfactants (tetradecyltrimethyl-ammonium bromide, $C_{14}TAB$, and cetyltrimethylammonium bromide, $C_{16}TAB$) containing fixed amounts of different quaternary salts (Me_4NBr, Et_4NBr, Pr_4NBr, Bu_4NBr, Bu_4PBr, ϕ_4PBr, tetra-*n*-amylammonium bromide (Am_4NBr), tetra-*n*-octylammonium bromide (Oc_4NBr), or propyltriphenylphosphonium bromide ($Pr\phi_3PBr$)). The addition of organic compounds (*n*-heptane, *n*-heptanol and *n*-heptylamine) caused viscosity increase when added in presence of the above salts beyond certain concentrations. However, with C_7NH_2, viscosity increase followed by a decrease (a peaked behavior) was observed with continuous addition of C_7NH_2. The peak positions and salt contents at the peak are found to be dependent on the length of

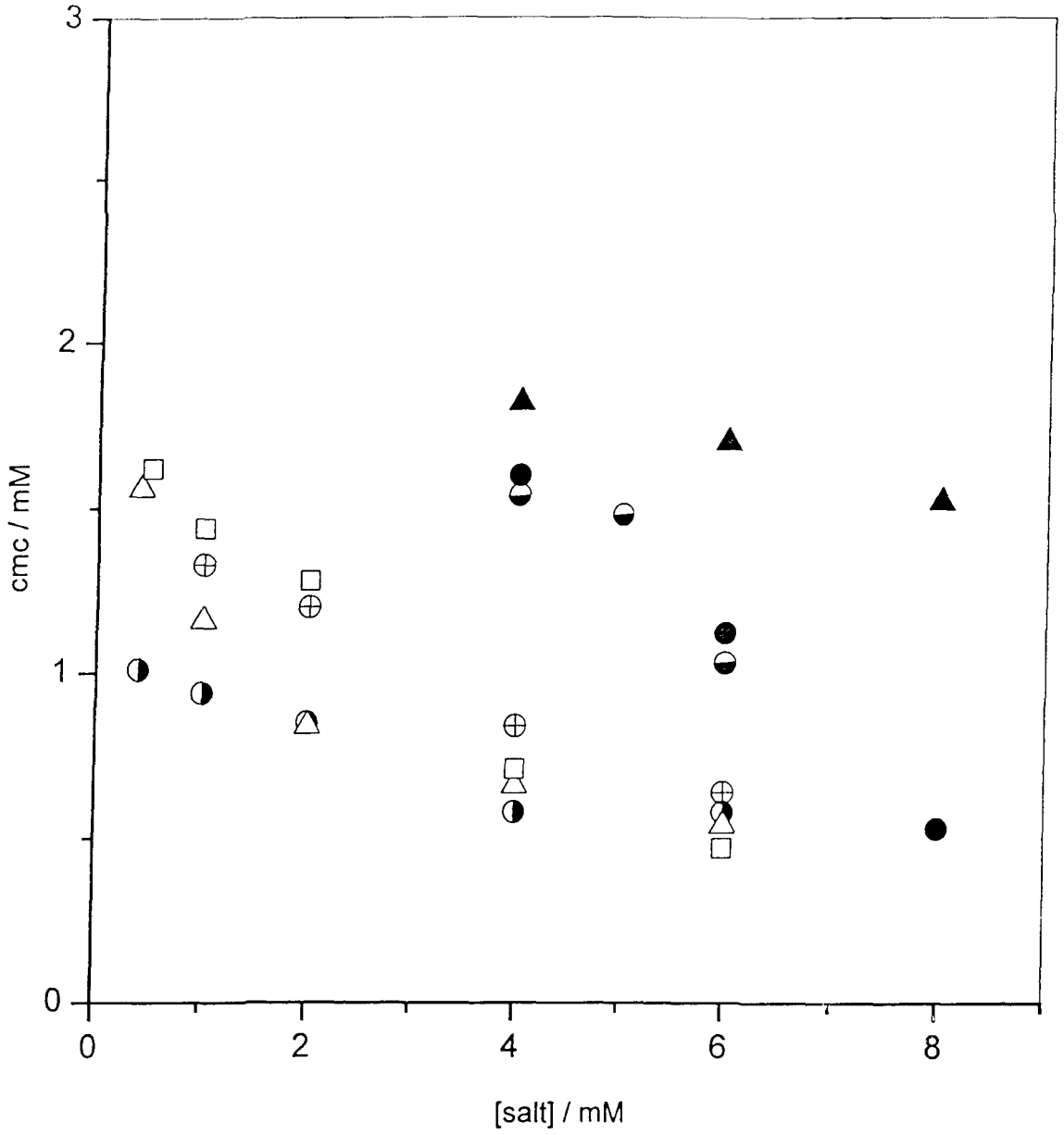

Fig. 1. Variation of cmc of SDBS with salt concentration: (▲), LiBr; (●), NaBr; (◒), NH_4Br; (◑), Me_4NBr; (△), Et_4NBr; (⊕), Pr_4NBr; (□), Bu_4NBr.

TABLE – 1.

Variation of the degree of dissociation (α) of SDBS micelles as a function of concentration and nature of the salts.

[Salt] / mM	LiBr	NaBr	NH_4Br	Me_4NBr	Et_4NBr	Pr_4NBr	Bu_4NBr	Bu_4PBr	ϕ_4PBr
0.4				0.81	0.80				
0.5							0.84	0.88	0.77
0.7									0.78
0.9									0.77
1.0				0.80	0.82	0.77	0.81	0.83	
2.0				0.79	0.78	0.78	0.85	0.84	
4.0	0.89	0.78	0.84	0.78	0.69	0.72	0.76		
5.0			0.81						
6.0	0.92	0.77	0.78	0.78	0.62	0.76	0.78		
8.0	0.91	0.75							

$\alpha = 0.86$ in water without any added salt.

alkyl/phenyl part of a particular salt but independent on the surfactant chain length. The overall behavior is discussed in the light of a change in the solubilization site of the organic additive caused by the presence of quaternary salts. Cavities in the quaternary salt coions present in the bulk solvent are proposed to be the new site of solubilization.[8]

The role of quaternary salts (Bu_4NBr, ϕ_4PBr, Bu_4PBr, $Pr\phi_3PBr$, Am_4NBr) as solubilization site modifiers of organic compounds in anionic micellar solutions (SDBS) has also been studied (**Chapter-V**). Here, another set of organic compounds (cycohexane, cyclohexanol, cyclohexylamine and aniline) was selected and the viscosity measurements were performed as mentioned in **Chapter-IV**. Cyclohexane, cyclohexylamine, cyclohexanol and aniline had marginal effects on the viscosity when added to 50 mM SDBS solutions having no salt. However, in the presence of Bu_4NBr (the other salts did not show any significant change in the relative viscosity, η_r), the effect was dependent on salt concentration and the nature of the additive. The effect has been interpreted on the basis of solubilization site alteration of the additive in the presence of Bu_4N^+ which acts as another counterion to the SDBS micelles.

The preceding three chapters show in detail how the micellization and solubilization are influenced by the presence of additives. It has been reported that the system SDBS + Bu_4NBr shows clouding under certain concentration and temperature ranges.[9] **Chapter VI** describes a preliminary phase study made on the above system to obtain various clear phase regions in the temperaure – [Bu_4NBr] phase diagram. Both upper (UCB) and lower consolute

boundaries (LCB) have been traced out.[10] Samples were selected on the basis of phase diagram study to perform small-angle neutron scattering measurements (SANS). Effects of varying [Bu_4NBr] and temperature on the SANS spectra were seen on samples belonging to both the regions. Also, for comparison, measurements were performed with pure SDBS and SDS micellar solutions. Hayter-Penfold model was used for data analysis.[11] Though both the surfactants possess dodecyl chain as the hydrophobic part, semi-minor axis (a) of SDS micelles is higher than the SDBS ones. This is explained in view of the presence of benzene ring in the headgroup region of SDBS micelles. Due to this benzene ring a repulsive interaction among π–electron clouds of SDBS monomers of the micelles would take place with increase in hydration forces.[7] This increased hydration would reduce the hydrophobic forces which assist the phenomenon of aggregation. SANS results obtained with the samples belonging to above UCB and below LCB regions show that the micelles grow with temperature increase when samples approach the LCB (Fig. 2) while micellar disintegration is observed in the former case (beyond UCB, Table 2).

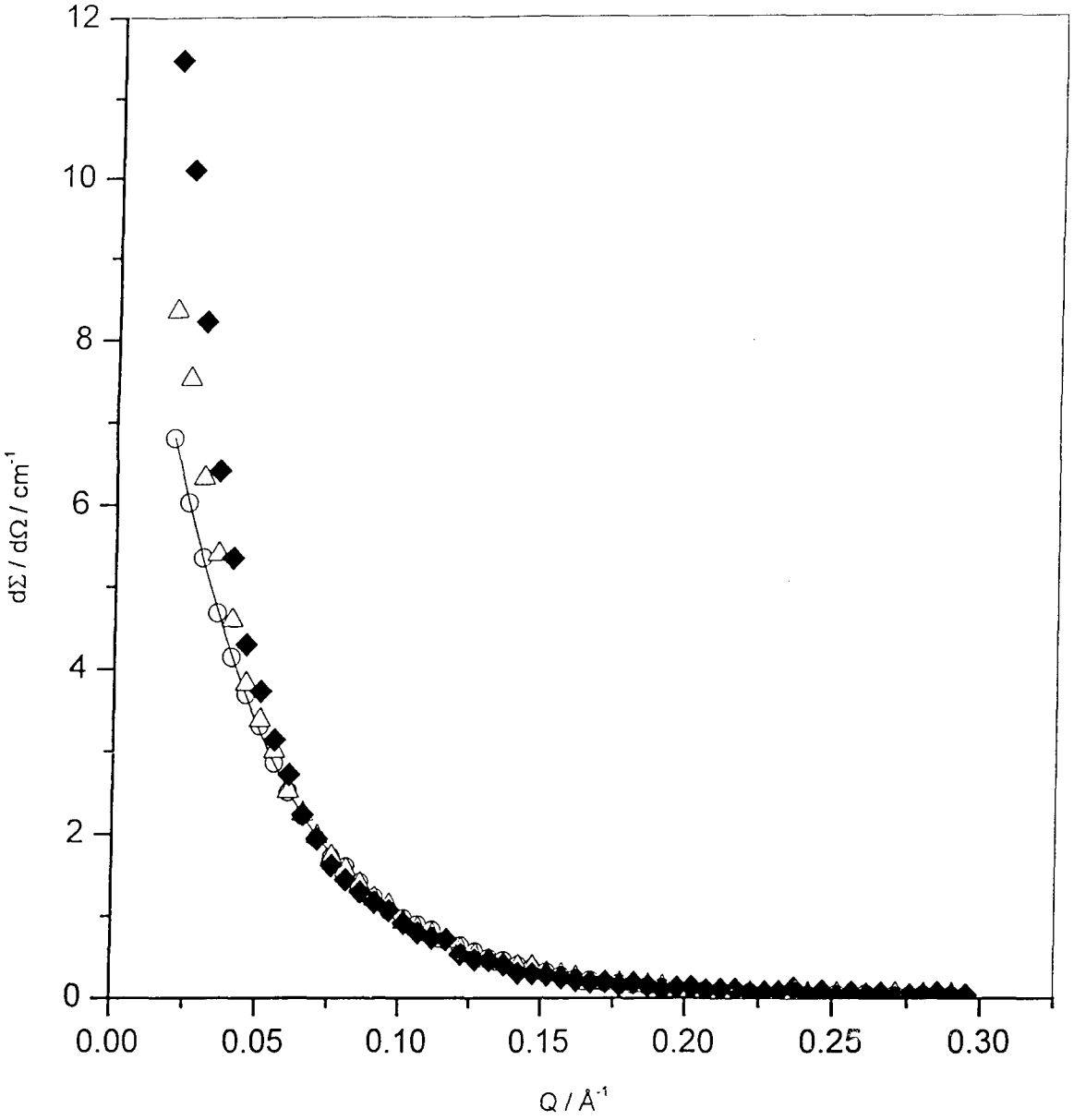

Fig. 2. SANS spectra from 50 mM SDBS + 32 mM Bu_4NBr system at different temperatures : 30 °C, (○); 40 °C, (△); 50 °C, (◆). Solid line is theoretical fit based on Hayter and Penfold-type analysis. Data for 40 °C and 50 °C could not be analyzed with the available model.

(The system belongs to the below LCB region where, contrary to a decrease in $d\Sigma/d\Omega$ in an above UCB system, $d\Sigma/d\Omega$ increased with increase in temperature —— the behavior is indicative of micellar growth).

TABLE - 2.

Micellar parameters for 100 mM SDBS + 39.5 mM Bu_4NBr[a] obtained from Hayter-Penfold - type analysis[b] at different temperatures.

Temperature / °C	N	α	*c* / Å	*a=b* / Å	*c/a*	χ_r^2
30	300	0.09	162.6	16.4	9.91	0.22
40	258	0.09	144.6	16.1	8.98	0.14
50	253	0.07	140.1	16.2	8.65	0.13
60	239	0.07	133.7	16.0	8.36	0.21
70	219	0.07	124.7	16.0	7.79	0.07
80	196	0.07	113.0	16.0	7.06	0.10

[a] the system belongs to the above UCB region.
[b] Ref.11.

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    (b) J. B. Hayter and J. Penfold, *Colloid Polym. Sci.*, **261**, 1022 (1983).

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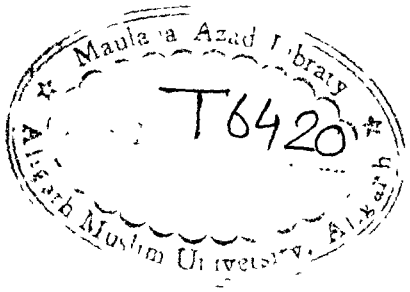
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My Humble Endeavor
To
My Grandfather
Shri K.L. Sharma

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH—202 002
(U. P.) INDIA

Phones {Ext. (0571) 7 0 3 5 1 5
{Int. 317, 318

Dated..May 10, 2006

CERTIFICATE

This is to certify that the thesis entitled "***Studies of Amphiphilic Systems***" is the original work carried out by **Daksha Sharma** under my supervision and is suitable for submission for the award of **Ph.D.** degree in **Chemistry**.

(Prof. Kabir-ud-Din)

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Daksha

(*Daksha Sharma*)

List of Publications

1. 'Micellization of Sodium Dodecylbenzenesulphonate in Aqueous Quaternary Bromides'.

   Sanjeev Kumar, **Daksha Sharma** and Kabir-ud-Din

   J. Surf. Sci. Technol., **18**, 25 (2002).

2. 'Role of Quaternary Bromides in Changing the Solubilization Site of *n*-Heptylamine in Cationic Micellar Solutions'.

   Sanjeev Kumar, **Daksha Sharma** and Kabir-ud-Din

   J. Surfact. Deterg., **6**, 339 (2003).

3. 'Quaternary Salts as Solubilization Site Modifiers of Organic Compounds in Anionic Micellar Solutions'.

   Sanjeev Kumar, **Daksha Sharma** and Kabir-ud-Din

   J. Surfact. Deterg., 7, 75 (2004).

Lists of Papers Presented/Accepted at Conferences

1. 'Change of Solubilization Site of *n*-Heptylamine in CTAB Micelles in Presence of Quaternary Ammonium Bromides'.

   89th Indian Science Congress, Lucknow, Jan. 3-7, 2002.

2. 'Micellization of Sodium Dodecylbenzenesulphonate in Aqueous Quaternary Bromides'.

   International Conference on Progress in Disperse Systems, Kolkata, Jan. 16-18, 2002.

3. 'Influence of Quaternary Bromides on the Viscosity Behavior of Sodium Dodecylbenzensulphonate Solutions'.

   90th Indian Science Congress, Bangalore, Jan. 3-7, 2003.

4. 'SANS from Aqueous SDBS–Tetra-*n*-butylammonium Bromide Samples Taken from Phase Regions in Contact with Lower and Upper Consolute Curves'.

   Conference on Neutron Scattering, Mumbai, Jan. 2-4, 2004.

CONTENTS

CHAPTER I

GENERAL INTRODUCTION

Many types of organic molecules with differing shapes and volumes form various kinds of molecular aggregates or assemblages in water. Surfactant monomers being one of them. Surfactant monomers can self-assemble in solutions to form a variety of microstructures.

The word surfactant, being a diminutive form of the phrase SURFace ACTive AgeNT, is a technical term that is why it does not appear in most dictionaries. Surfactants are vital components in biological systems, form key ingredients in consumer products, and play an important role in many industrial processes. Cell membranes owe their structure to the aggregation of surfactants known as lipids which form a major component of the membrane.

Among natural forces, the hydrophobic-lipophilic effect is one of the most important and necessary forces for formation of spatially ordered semimicroscopic assemblies of amphiphilic molecules, e.g., association colloids, vesicles, biological membranes, monolayers, proteins, DNA, and living cells.[1-4] Association colloids are dynamic aggregates of surfactants such as micelles (direct and reverse) and microemulsions (o/w and w/o). Micelles have attracted significant attention because of their ability to function as encapsulating and biomimetic systems.

The applications of surfactants in medical, pharmaceutical, cosmetic and pesticidal industries are all too familiar. Surfactants have been shown to be helpful in converting solar light into chemical fuel, and such a direct energy conversion is of tremendous value. In the last few decades, there has been a great deal of research activity in understanding the role of surfactants in enhanced oil recovery. The use of microemulsions (water-oil transparent dispersions stabilized by mixed film of surfactant(s)) as fuels, as solvents for coatings, and as cleaning agents all open up intriguing possibilities.

Surfactants have become the subject of intense investigation by researchers in the fields of chemical kinetics and biochemistry also because of the unusual properties of the aggregated forms (e.g., micelles) of these materials.

Surfactants and their Classification

A surface-active-agent[5] is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface (or interfacial) free energies of those surfaces (or interfaces).[6,7]

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent as lyophobic group (or hydrophobic when the solvent is water), together with a group that has strong attraction for the solvent, called the lyophilic group (or hydrophilic). This is known as amphipathic structure. They are amphiphilic organic or organometallic compounds.

The nonpolar or hydrophobic portion of the molecule is most commonly a flexible chain hydrocarbon. It can be of different lengths, can contain unsaturated portions or aromatic moieties and can be branched or consist of two or more chains. The polar or hydrophilic region of the molecule may carry a positive or negative charge giving rise to cationic or anionic surfactants, respectively, or may be composed of a polyoxyethylene chain as in the case of nonionic surfactants.

(i) Cationic Surfactants

The most prevalent cationic surfactants are based upon quaternary nitrogen. Alkyl ammonium halides and tetraalkylammonium halides are the most numerous in this class. The cation of the compound is surface active species.

Examples

Cetyltrimethylammonium bromide, CTAB $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$

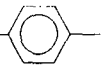
Dodecylpyridinium chloride, DPC $CH_3(CH_2)_{11}N^+C_5H_5Cl^-$

The positive charge on the headgroup gives the surfactant a strong substantivity on negatively charged fibers, such as cotton and hair, and they are therefore used as fabric and hair conditioners.

(ii) Anionic Surfactants

These include the traditional soaps ($-CO_2^-$) and the early synthetic detergents, the sulfonates ($-SO_3^-$) and the sulfates ($-OSO_3^-$). All of these still feature extensively in cleaning formulations. The major advantage of the sulfonates and sulfates over the carboxylates is their greater tolerance of divalent metal ions in hard water.

Examples

Sodium dodecylbenzenesulfonate, SDBS $CH_3(CH_2)_{10}CH_2$—  $SO_3^-Na^+$

Sodium dodecylsulfate, SDS $CH_3(CH_2)_{11}OSO_3^-Na^+$

They have good particulate soil removal and dispersion properties and generally have high foaming characteristics. A major use of these surfactants is in household detergents and other cleaning products.

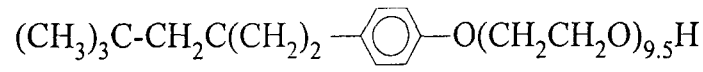
(iii) Non-ionic Surfactants

These are dominated by the ethoxylates, $-(OCH_2CH_2)_nOH$. They are used extensively in low-temperature detergency and as emulsifiers. This class of surfactants also includes several so-called semi-polar compounds such as the amine oxides, sulfoxides and phosphine oxides. These surfactants are structurally analogous to anionic and cationic surfactants,

except that the headgroup is uncharged. The water-soluble moiety of this type can contain hydroxyl groups or a polyoxyethylene chain.

Examples

Polyoxyethylene *p-t*-octylphenol, TX-100



Polyoxyethylene monohexadecyl ether $CH_3(CH_2)_{15}(OCH_2CH_2)_{21}OH$

(iv) Zwitterionic Surfactants

This type can behave as either an anionic, nonionic, or cationic species, depending on the pH of the solution. These are used in the form of betaines ($-N^+(CH_3)_2CH_2CO_2^-$) or sulfobetaines ($-N^+(CH_3)_2CH_2SO_3^-$). These compounds are milder on the skin than the anionics and have especially low eye-sting effects, which leads to their use in toiletries and baby shampoos.

Examples

N-Dodecyl-N,N-dimethylglycine $CH_3(CH_2)_{11}N^+(CH_3)_2CH_2COO^-$

3-(Dodecylmethylammonio)propane-1-sulfonate

$CH_3(CH_2)_{11}N^+H(CH_3)CH_2CH_2CH_2SO_3^-$

Among the naturally occurring surfactants in this class are the important lecithins or phosphatidyl cholines, which have the headgroup $-O-PO_3^- - CH_2CH_2-N^+(CH_3)_3$. The physiologically important bile salts have rigid structures as opposed to the flexible chains of soaps and detergents.

(v) Gemini Surfactants

These surfactants, in contrast to their more traditional (single-chain/ single polar headgroup) counterparts, are made of two hydrophobic chains

and two hydrophilic headgroups linked by a spacer group. The spacer can be flexible or rigid, hydrophobic or hydrophilic. Such type of surfactants are known as dimeric or gemini. The surfactant properties are very different from those of the corresponding monocationic compound and are strictly dependent on the spacer, whose nature can be very different. Few of them possess exceptional properties, such as very low critical micellar concentration, high viscoelasticity, and an enhanced propensity for lowering the oil-water interfacial tension in comparison to their single-chain analogs.[8]

Examples

1,5-Bis(hexadecyl-N,N-dimethylammonium bromide)pentane

$$H_{33}C_{16}Me_2N^+(CH_2)_5\ N^+\ Me_2C_{16}H_{33}$$
$$\quad\quad Br^- \quad\quad Br^-$$

1,4-Bis(dodecyl-N,N-dimethylammonium bromide)-2-butanol

$$H_{25}C_{12}Me_2N^+CH_2CHOHCH_2CH_2N^+Me_2C_{12}H_{25}$$
$$\quad\quad Br^- \quad\quad\quad\quad Br^-$$

Geminis are used as promising surfactants in industrial detergency and have shown efficiency in skin care, antibacterial property, metal-encapped porphyrazine and vesicle formation, construction of high-porosity materials, etc. Gemini surfactants are of interest as they provide a system where aggregation behavior can be controlled by varying the spacer while keeping the length of the tail fixed. Gemini sufactants with a great variety of chemical structures have been obtained by acting on the nature of the headgroup and spacer group.[8]

An exhaustive list of both synthetic and naturally occurring surfactants is available. Their preparation and properties in general have been given in

the excellent monograph of Fendler and Fendler.[9] Zana[10] has presented details regarding the geminis.

Critical Micelle Concentration

Surfactant molecules self-aggregate into supermolecular structures when dissolved in water or oil. The simplest aggregate of these surfactant molecules is called a micelle.[2,11]

The co-existance of two opposite types of behavior (hydrophilic and hydrophobic) inside the same molecule is the origin of local constraints which lead to spontaneous aggregation.

In dilute aqueous solution, surfactants behave as simple organic molecules. At higher concentration, however, they no more show the ideal behavior of their dilute solutions. These deviations are different from those exhibited by simple strong electrolytes. In the higher concentration range, the amphiphiles form micelles, which change some of the physical properties of the surfactant solutions. The related physical properties are interfacial tension, electrical conductivity, solubility, electromotive force, pH, transport (like viscosity) and spectroscopic properties. The concentration at which the aggregates are formed and manifest distinct physical properties is called the critical micellar concentration (cmc). This change occurs over a narrow concentration range rather than at a precise point[12] (Fig. 1.1). The magnitude of this range depends somewhat on the physical property being measured. The discontinuity in the property of the solution can be used to identify the cmc. Some of the techniques used frequently to identify the cmc are surface tension, osmotic pressure, *electrical conductivity*,[13] *dye solubilization*,[14,15] ^1H *NMR*,[16,17] *light* scattering,[18] fluorimetry,[19] interference refractometry,[20] etc. Different

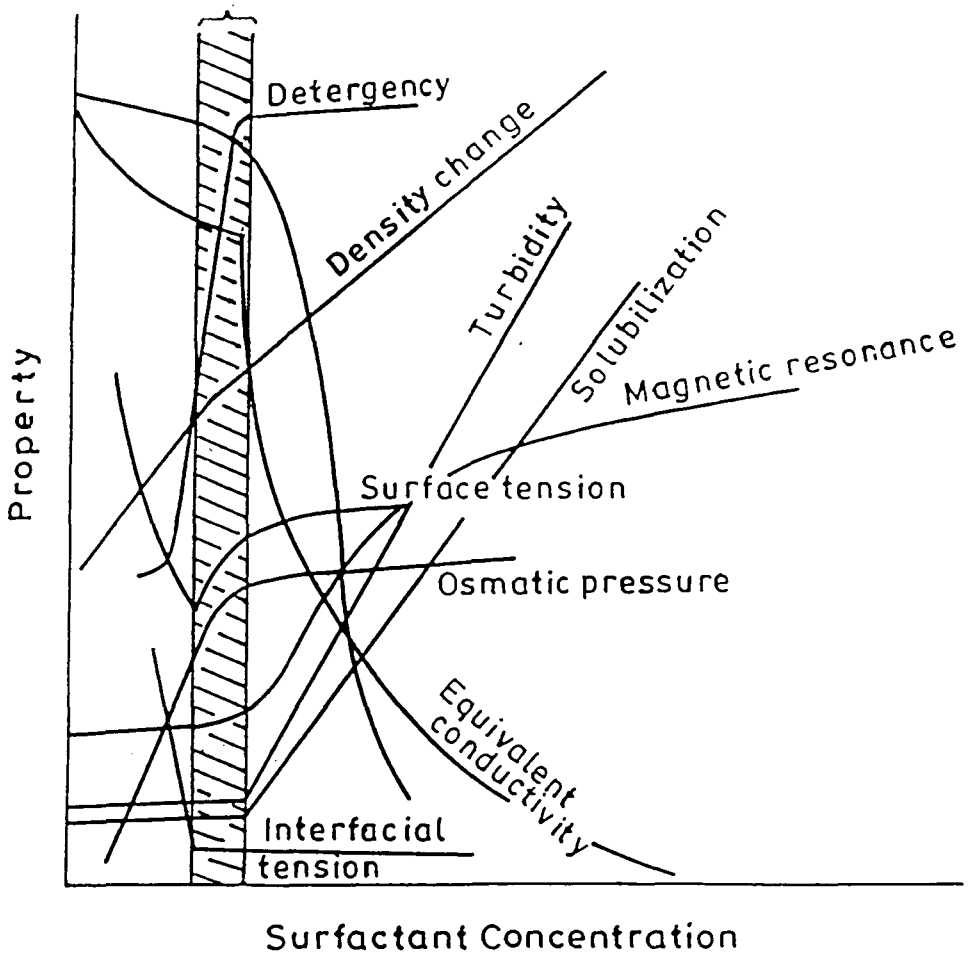


Fig. 1.1. Variation of physical properties with surfactant concentrations.

experimental methods available for determining the cmc are listed in the compilations of Shinoda *et al.*,[21] Elworthy *et al.*,[22] and Mukerjee and Mysels.[23] The latter authors have also compiled cmc values and have critically evaluated different methods used for their determination.

Micelles are not static species but rather exist in a dynamic equilibrium. They are noncovalently bonded macromolecular aggregates that are of highly dynamic character. The alkyl chains constituting the micellar core are in constant motion and the water molecules, the counterions and the surfactant ions are continually and reversibly exchanging between micelle bound and free states.[2] In an aqueous surfactant solution, micelles break and reform at a fairly rapid rate, in the range of milliseconds.[24-26]

On transferring the monomer into the micelle, the high energy of the hydrocarbon/water interface is lost, as the chain is now in contact with others of a like nature. As Hartley[27] points out, there is no repulsive force between water and the hydrocarbon chain; rather there is a strong adhesion between water molecules, and the hydrocarbon tends to be squeezed out from close contact with them.

Transfer of monomer into the micelle also means that the structuring of water around the hydrocarbon part of the monomer is lost; therefore, an ordered state has become a disordered one with regard to the water, meaning that there is a positive entropy change and a decrease in free energy. Loss of hydrocarbon/water interfacial energy and loss of water structure thus provide driving forces for the formation of micelles.

A second factor is that there is a loss of freedom, particularly of translational freedom, in placing a monomer in a micelle. This disorder-to-

order transition gives a negative entropy change, which will oppose the positive entropy changes occurring from loss of water structure. The overall decrease in free energy due to loss of hydrocarbon/water interfacial energy and water structure outweighs the free energy rise due to electrical work and translational freedom losses, giving a stabilizing of the micelles.

For ionized surfactants, the bringing together of monomers into a micelle means that work has to be done against the electrostatic repulsions between similarly charged polar headgroups, which is one factor opposing the formation of micelles. Nonionic surfactants, for which no electrical forces are expected to oppose micellization, form micelles at lower concentrations than ionic ones. Forces opposing micellization for the ionic surfactants may also arise from solvation changes of headgroups, or entropic effects when the flexible hydrophilic (polyoxyethylene) chains are brought together in the micelle.

As already pointed out, dynamic association-dissociation equilibria exist in micellar solutions. However, the theoretical treatment of micelles depends on whether the micelle is regarded as a chemical species or as a separate phase. The mass action model, which has been used ever since the discovery of micelles, takes the former point of view,[28-33] whereas the phase separation model regards micelles as a separate phase.[34-38] To apply the mass action model strictly, one must know every association constant over the whole stepwise association from monomer to micelle, a requirement almost impossible to meet experimentally. Therefore, this model has the disadvantage that either monodispersity of the micelle aggregation number must be employed or numerical values of each association constant have to be measured.[39-44] The phase separation model, on the other hand, is based on

the assumption that the activity[34,45-50] of a surfactant molecule and/or the surface tension[21,37,51,52] of a surfactant solution remain constant above the cmc. In reality, neither quantity remains constant,[32,53,54] so this model is also not strictly correct. Another new approach rests on the application of the thermodynamics of small systems[55] to micellar systems. In any case, over the past decade the nature of ionic micelles has been made clearer from studies of the activity of both surfactant ions[47-50,56,57] and counterions,[46,47,49,50,56,58] owing to development of new electrochemical techniques.

Normal Micelles

In pure water ionic surfactants form small liquid-like droplets, the so-called micelles, above a certain concentration. Such micelles are considered as roughly spherical (Fig. 1.2).[21,22,59] In polar solvents (i.e., water, formamide, 1-2 diols, etc),[60-65] monomer tails huddle in the core of the micelle, and the polar head groups project outwards into the polar bulk solution and locate at the micelle-water interface such that the hydrophobic tails are shielded from water. Electrical charge on a micelle is neutralized by counterions in the electrical double layer around it. The first layer immediately adjacent to its surface is called the Stern layer.[66] In this layer the counterions are adsorbed so strongly that there is no thermal agitation and they migrate together with the colloidal micelle in an electrical field. According to the most widely accepted model, the headgroups of surfactant molecules also situate in this layer. The remainder of the double-layer is called the diffuse (Gouy-Chapman) layer. The core radius is about the length of the fully extended alkyl chain of the amphiphile (~10-28 Å) (Fig. 1.3). The core is believed to consist of two regions, namely the inner core and outer core. There is also another defined region within micelles called

Fig. 1.2. Schematic Structure of a spherical micelle.

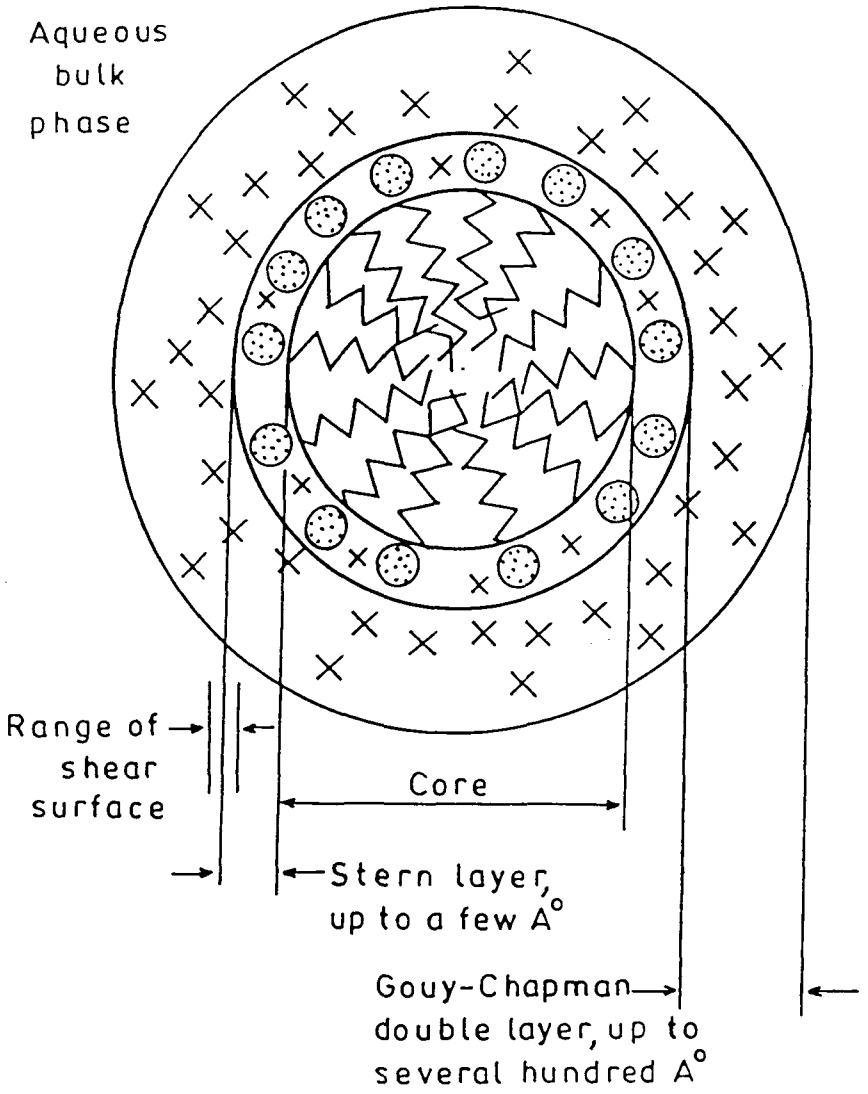


Fig. 1.3. A two dimensional schematic representation of the regions of a spherical ionic micelle. The counterions (×), the headgroups (◎), and the hydrocarbon chains (∧∧∧) are schematically indicated to denote their relative locations but not their number, distribution, or configuration.

palisade layer (mantle) which includes the headgroups and the first few methylene groups. On the basis of the Hartley model, the overall volume of a micelle is approximately twice that of Stern layer.[67-69] Micelles of ionic surfactants are aggregates composed of a compressive core surrounded by a less compressive surface structure,[70] and with a rather fluid environment.[71] In order to explain the relatively low degree of micelle ionization, Stigter and Mysels suggested that the micellar surface is rough,[72] and Stigter placed the hydrocarbon core-water interface at 0.4-1.2 Å from the center of the α-carbon atoms of ionic surfactants.[73] The water activity at the Stern layer of ionic micelles is not much less than in bulk water.[74] The rate of water reorientation at the ionic micellar surface is typically two to three times slower than in pure water, and the average life time of water molecules associated with micelles is between 6 and 37 ns.[75] The nonionic micelles arrest water molecules at the palisade layer by hydrogen bonding of water with the polyethylene oxide groups.[76] Water may be entrapped in this region.

Ionic micelles bind counterions selectively, and their solution properties such as aggregate size and shape, phase stability, the binding of ions and molecules, and their effects on the rates and equilibria of chemical reactions are sensitive to counterion concentration and type.[3,77-84] No doubt, counterions are 'bound' primarily by the strong electrical field created by the headgroups but also by specific interactions that depend upon headgroup and counterion type. Counterions are assumed to be free to move within the interfacial region and to exchange rapidly with counterions in the surrounding aqueous phase.[85-87]

Specific coutnerion effects on a variety of micellar properties generally follow a Hofmeister series,[59] i.e., for counterions of the same valence, the size of the effect increases with counterion size (crystal radius)

and the ease of dehydration of the counterion.[69,82,88,89] However, specificity may also depend upon hydrogen-bonding interactions between hydrated counterions and headgroups or the partial disruption of the hydration layers of the headgroups and counterions, and the possibility that a fraction of the counterions are site-bound to surfactant headgroups, e.g., contact ion-pair formation, cannot be excluded.

Reverse Micelles

Aggregates are also formed in apolar solvents. In such cases headgroups of surfactant molecules locate inside to form a polar core and hydrocarbon tails are directed towards the bulk solvent to form the outside shell of the micelle (Fig.1.4). These are called reverse or inverted micelles.[90-100] If there is any water in the medium, it will be entrapped in the core.[92-95] This surfactant-solubilized-water is often referred to as a water pool and reverse micelles are sometimes called microemulsions (depending upon the degree of swellenity). They are able to solubilize relatively large amount of water in their cores and this enables them to solubilize water soluble substances in nonpolar solvents. They are also reported to form near- and supercritical fluids.[101,102] Reverse micelles are very small, with an aggregation number seldom exceeding 10 due to the lack of a strong driving force; water is prerequisite for the formation of reverse micelles, and the driving force for the formation of reverse micelles is dipole-dipole interactions.[5,103-111]

The inner cavity of reverse micelles have been compared with the active sites of enzymes,[112,113] water in reverse micelles is expected to behave very differently from ordinary water because of extensive binding and orientation effects induced by the polar heads forming the water core.[114] Reverse micelles are able to solubilize hydrophilic molecules like enzymes

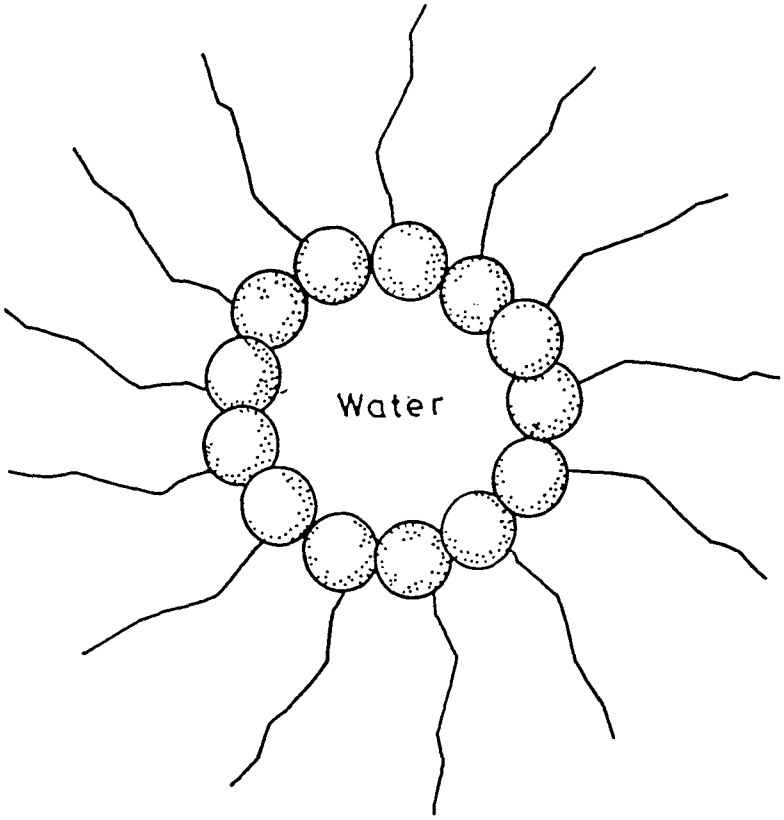


Fig. 1.4. Schematic structure of a reverse micelle.

and plasmids that are much larger than the original water pool diameter. Such micelles can be viewed as novel microreactors whose physical properties can be controlled through the water content.

Mixed Micelles

The formation of micelles from more than one chemical species gives rise to what are known as mixed micelles. In the simplest case, binary or ternary mixtures of surfactants of similar, but not identical, chain lengths may be studied and the thermodynamics of this type of micelle formation has been described.[21,115] When two or more types of surfactants are in solution, a complex balance of intermolecular forces is responsible for the formation of mixed micelles against the formation of micelles constituted by surfactants of only one type.[116] Mixed micelles are also formed when low molecular weight solutes are solubilized by micelles of surfactants containing a relatively larger nonpolar side chain. The solubilized substance, also called a penetrating additive,[117] may be located in both the hydrocarbon core[118] and in hydrophilic mantle.[119]

Specific interactions (synergistic or antagonistic) between surfactants result in solutions of surfactant mixtures having micellar and phase behavior properties which can be significantly different from those of the constituent single surfactants.

Clint[120] proposed a phase separation model to describe the phenomenon of mixed micelle formation. According to the model, ideal mixing of the surfactants in the micellar phase is assumed which permits calculation of the critical micelle concentration (cmc) of the mixed entities in terms of the overall composition of the combined component and the critical micelle concentrations of the individual surfactants. The ideal

mixing theory has been quite successful in explaining the properties of surfactants having similar structures but can hardly account for the characteristics of mixed systems of dissimilar structural features. Theoretical treatments were, therefore, developed on the basis of regular solution theory with provisions for specific interactions between the two types of surfactants forming the micelles. Rubingh[121] formulated a theoretical treatment to relate the monomer concentration to the micellar composition.

The descriptions of mixed surfactant solutions available in literature are mostly based on Rubingh's approach mainly because it includes a specific interaction parameter β giving a measure of the interaction of the surfactant species in solution. Although found to be reasonably satisfactory in many cases,[122,123] the theory was criticized on thermodynamic grounds. Motomura *et al.*[124] proposed a mixed micellar model on thermodynamic considerations claiming it to be a better description of mixed surfactant solutions. Later, a molecular thermodynamic model for mixed surfactant systems was developed.[125-127]

Further, mixed micelles provide better performance characteristics in their applications than those consisting of only one type of surfactant.[116,128] They also offer a behavior different than that expected with respect to the pure component solution; e.g., increasing surface activity yields a decrease in the cmc and surface tension, γ, of particular interest from both theoretical and technological standpoints (pharmaceutical, food, detergency, cosmetics, micellar solubilization, and enhanced oil recovery, etc.).[116,128] It is thus necessary to enlarge the scarce database of micelle properties and parameters for mixed systems of surfactants of identical hydrophobic chain and different polar heads, given that it will contribute to better knowledge,

both theoretical and practical, and prediction of the properties of mixed systems.

The occurrence of mixed surfactants and hence mixed micelles are common in industrial, pharmaceutical and biological fluids; physico-chemically, they work better than pure surfactants in solution.

Factors Affecting the Value of Critical Micellar Concentration

(i) ***Structure of the surfactant***

(a) hydrocarbon chain length

In aqueous medium, the cmc decreases as the hydrocarbon chain length increases. For the same head group, compounds containing longer hydrocarbon chains form micelles at lower concentrations than those containing short chains. The decrease of interfacial free energy on micellization is more for longer chains than for short ones.

The cmc is related to the number (n) of carbon atoms in a straight hydrocarbon chain by[129]

$$\log \text{cmc} = A - Bn \qquad (1.1)$$

where A and B are constants for a homologous series; Shinoda *et al.*[21] have listed values of A and B for various homologous series.

A generally used rule for ionic surfactants is that the cmc is halved by the addition of one methylene group to a straight-chain hydrophobic group attached to a single terminal hydrophilic group. For nonionics, the decrease with increase in the hydrophilic group is somewhat larger, an increase by two methylene units reducing the cmc to about one-tenth its previous value.

A phenyl group that is part of a hydrophobic group with terminal hydrophilic group is equivalent to about three and one-half methylene groups.

When the number of carbon atoms in a straight-chain hydrophobic group exceeds 16, however, the cmc no longer decreases so rapidly with increase in the length of the chain and when the chain exceeds 18 carbons it may remain substantially unchanged with further increase in the chain length.[130] This may be due to the coiling of these long chains in water.[33] Lengthening of the hydrocarbon chain causes an increase in the micelle size.

(b) presence of C = C and cis - trans isomer

When carbon-carbon double bonds are present in the hydrophobic chain, the cmc is generally higher than that of the corresponding saturated compound, with the *cis* isomer generally having a higher cmc than the *trans* isomer.

(c) introduction of a polar group

Polar group such as –O– or –OH into the hydrophobic chain generally causes a significant increase in the cmc in aqueous medium at room temperature, the carbon atoms between the polar group and the hydrophilic head appearing to have about one-half the effect on the cmc that they would have were the polar group absent.

When the polar group and the hydrophilic group are both attached to the same carbon atom, that carbon atom seems to have no effect on the value of the cmc.

The replacement of a hydrocarbon-based hydrophobic group by a fluorocarbon-based one with the same number of carbon atoms appears to cause a decrease in the cmc. By contrast, the replacement of the terminal methyl group of a hydrocarbon-based hydrophobic group by a trifluoromethyl group has been shown to cause the cmc to increase.

(d) the hydrophilic group

In aqueous medium, ionic surfactants have much higher cmc's than nonionic surfactants containing equivalent hydrophobic groups; 12-carbon straight-chain ionics have cmc's of *ca.* 1 x 10^{-2} M, whereas nonions with the same hydrophobic group have cmc's of *ca.* 1 x 10^{-4} M.

Zwitterionics appear to have about the same cmc's as ionics with the same number of carbon atoms in the hydrophobic group. As the hydrophilic group is moved from a terminal position to a more central position, however, the cmc increases.

It has been found[73] that the cmc is higher when the charge on an ionic hydrophilic group is closer to the α-carbon atom of the (alkyl) hydrophobic group. This is explained as due to an increase in electrostatic self-potential of the surfactant ion, when the ionic headgroup moves from the bulk water to vicinity of the nonpolar micellar core during the process of micellization; work is required to move an electric charge closer to a medium of lower dielectric constant.

The order of decreasing cmc in some *n*-alkyl ionics was : aminium salts > carboxylates (with one more carbon atom in the molecule) > sulfonates > sulfates. This same order had been noted earlier.[129] Surfactants containing more than one hydrophilic group in the molecule show larger cmc's than those with one hydrophilic group and the equivalent hydrophobic group. Substitution of hydrogen atoms on an element of the hydrophilic group by small (1-2 carbon) alkyl or alkanol groups, (not between the hydrophilic and hydrophobic groups), such as the replacement of hydrogens of an amino group by methyl groups, appears to cause only a slight increase, if any, in the cmc. For the usual type of polyoxyethylenated nonionic (in which the hydrophobic group is a hydrocarbon residue), the cmc in aqueous

medium decreases with decrease in the number of oxyethylene units in the polyoxyethylene chain, since this makes the surfactant more hydrophobic. However, the change per oxyethylene unit is much smaller than that per methylene unit in the hydrophobic chain. The greatest decrease per oxyethylene unit seems to be obtained when the polyoxyethylene chain is short and the hydrophobic group is long.

(e) the position of the head group

The closer the headgroup to the centre of the chain, the higher the cmc; due to the two branches of the chain partially shielding one another (interfacial energy effects are smallest).

(f) the counterion in ionic surfacants

The critical micelle concentration in aqueous solution reflects the degree of binding of the counterion to the micelle. Increased binding of the counterion, in aqueous systems, causes a decrease in the cmc of the surfactant. The extent of binding of the counterion increases with increase in its polarizability and valence, and decrease with increase in its hydrated radius. Thus, in aqueous medium, for the anionic dodecyl sulfates, the cmc decreases in the order $Li^+ > Na^+ > K^+ > Cs^+ > (CH_3)_4N^+ > (C_2H_5)_4N^+ > Ca^{++}$, Mg^{++}. When the counterion is a cation of a primary amine, RNH_3^+, the cmc decreases with increase in the chain length of the amine.[131] For the cationic dodecyltrimethylammonium and dodecylpyridinium salts, the order of decreasing cmc in aqueous medium is $F^- > Cl^- > Br^- > I^-$.[33,132,133] The depression of the cmc from Li^+ to K^+ is small, but for the other counterions it is quite substantial.

(ii) Pressure

Many reports have appeared on the effect of pressure on micelle formation of the ionic[134-139] and nonionic surfactants.[140] With pressure cmc

of ionic surfactants increases upto 1000 atm followed by a decrease above this pressure.[141-146] Such behavior has been rationalized in terms of solidification of the micellar interior,[141] increased dielectric constant of water,[142] and other aspects related to water structure.[143] For nonionic surfactants, the cmc value increases monotonously and then levels off with increasing pressure. La Mesa[147] has also discussed the effect of pressure on the cmc. It has been suggested that the soap molecules when present in the micelle are in a more expanded condition than when present as the monomer in solution, so that the initial effects of pressure tend to compress the micelle and mitigate against the increased freedom of the monomer in the micelle, thus giving a rise in cmc. The decrease in cmc on increasing the pressure above 1000 atm may be due to an increase in the dielectric constant of water, making less electrical work necessary to bring a monomer into a micelle.

(iii) *Temperature*

The effect of temperature on the cmc of ionic surfactants in aqueous medium is complex, the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature. Temperature increase causes decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the cmc increases or decreases over a particular temperature range. For bivalent metal alkyl sulfates, the cmc appears to be practically independent of the temperature.[148] For nonionic surfactants the cmc decreases with temperature upto the highest value measured, indicating that desolvation

effects on both hydrocarbon and polyoxyethylene chains of the monomer may be so large that they outweigh possible effects of thermal agitation in breaking up the micelles.

The micelle size of ionic detergents decreases with temperature,[149] an effect again due to thermal agitation. Micelles of non-ionic detergents increase rapidly in size with an increase in temperature[150-152] which may be due partially to increased monomer hydrophobicity and partially to geometric considerations based on different configurations of polyoxyethylene chains at different temperatures affecting the mode of packing of the monomers in the micelle.

For SDS in water the minimum in cmc occurs around 298 K,[153] whereas for hexyltrimethylammonium bromide it occurs at 303 K.[154] For nonionic surfactants, cmc minimum appears to be at 323 K. La Mesa[147] used the reduced variable treatment to explain the temperature dependence of cmc. Muller[155] derived a better analytical expression in terms of heat capacities of micellization to describe the temperature dependence of cmc. The temperature of minimum cmc for both nonionic and ionic surfactants increases as the hydrophobicity of surfactants decreases.[156] cmc's of alkyltrimethylammonium bromides in water are reported even upto 433 K.[157,158] The position of the minimum has thermodynamic significance. The cmc is a measure of the standard free energy change for micellization and can be written as

$$\Delta G^{o}_{m} = - RT \, ln \, (cmc) \qquad (1.2)$$

Therefore, the minimum in cmc represents a minimum in the free energy of micellization.

(iv) ***pH***

Where surfactant molecules contain ionizable groups such as $-NH_2$, $-(CH_3)_2N\rightarrow O$, and –COOH, the degree of the dissociation of the polar group will be very dependent on pH.[159] In general, the cmc will be high at pH values where the group is charged (low pH for $-NH_2$ and $-(CH_3)_2 N\rightarrow O$, high pH for –COOH) and low when uncharged. Some zwitterionic surfactants become cationic at low pH, a change that can be accompanied by a rapid rise in the cmc[160] or a more modest rise[161] depending on the structure and hence hydrophilicity of the zwitterionic form.

(v) ***Electrolyte***

In solutions of increasing ionic strength, the forces of electrostatic repulsion between headgroups in a micelle are considerably reduced, enabling micelles to form more easily, that is, at lower concentration. In other words, the cmc will be reduced by adding electrolyte. The effect being more pronounced for anionic and cationic than for zwitterionic surfactants and more pronounced for zwitterionics than for nonionics.

Experimental data indicate that for the first two classes of surfactants, the effect of the concentration of electrolyte is given by the following equation[162]

$$\log C_{cmc} = - a \log C_i + b \qquad (1.3)$$

where a and b are constants for a given ionic head at a particular temperature and C_i is the total (monovalent) counterion concentration in moles per liter.

The depression of the cmc in these cases is due mainly to the decrease in the thickness of the ionic atmosphere surrounding the ionic headgroups in the presence of the additional electrolyte and the consequent decreased electrical repulsion between them in the micelle.

For nonionics and zwitterionics the preceding relationship does not hold. Instead, the effect is given better by the equation.[163-165]

$$\log C_{cmc} = -KC_s + \text{constant} \quad (C_s<1) \qquad (1.4)$$

where K is a constant for a particular surfactant, electrolyte and temperature and C_s is the concentration of electrolyte in moles per liter. The change in the cmc of nonionics and zwitterionics on the addition of electrolyte has been attributed[33,165,166] mainly to the 'salting out' or 'salting in' of the hydrophobic groups in the aqueous solvent by the electrolyte, rather than to the effect of the latter on the hydrophilic groups of the surfactant.

The effects of the anion and the cation in the electrolyte are additive and appear to depend on the radius of the hydrated ion, that is, the lyotropic number; the smaller the radius of the hydrated ion, the greater the effect. Thus the order of effectiveness in decreasing the cmc is ½ $SO_4^{--} > F^- > BrO_3^- > Cl^- > Br^- > NO_3^- > I^- > CNS^-$ and $NH_4^+ > K^+ > Na^+ > Li^+ >$ ½ Ca^{++}.[165,167] Tetraalkylammonium cations appear to increase the cmc, the order of effectiveness being : $(C_3H_7)_4N^+ > (C_2H_5)_4N^+ > (CH_3)_4N^+$. This is the order of their effectiveness in 'salting in' of nonpolar solutes.[165]

(vi) ***Organic additives***

Polar organic compounds, such as alcohols and amides affect the cmc at much lower liquid phase concentrations. Shorter-chain members of the class are probably adsorbed mainly in the outer portion of the micelle close to the water-micelle 'interface'. The longer-chain members are probably adsorbed mainly in the outer portion of the core, between the surfactant molecules.[21,168-173]

Adsorption of the additives in these fashions decreases the work required for micellization, in the case of ionic surfactants probably by decreasing the mutual repulsion of the ionic heads in the micelle.

Depression of the cmc appears to be greater for straight-chain compounds than for branched ones and increases with chain length to a maximum when the length of the hydrophobic group of the additive approximates that of the surfactant.[174]

Additives that have more than one group capable of forming hydrogen bonds with water in a terminal polar grouping appear to produce greater depressions of the cmc than those with only one group capable of hydrogen bonding to water.[174]

Just as polar compounds that are believed to penetrate into the inner portion of the core produce only small depressions of the cmc, so, too, hydrocarbons, which are solublized in the inner portion of the core, decrease the cmc only slightly. Very short-chain polar compounds (e.g., dioxane and ethanol), at low bulk phase concentrations, also depress the cmc, but the effect here, too, is small.[175] In these compounds, adsorption probably occurs on the surface of the micelle, close to the hydrophilic head. There is another class of compounds that change the cmc by modifying the interaction of water with the surfactant molecule or with the micelle, doing this by modifying the structure of the water, its dielectric constant, or its solubility parameter (cohesive energy density). Members of this class include urea, formamide, N-methylacetamide, guanidinium salts, short chain alcohols, dioxane, ethylene glycol and other polyhydric alcohols such as fructose and xylose.[168,176,177]

(vii) ***Solvent effect***

The cmc of hexaoxyethylene dodecyl ether in cyclohexane saturated with water increases markedly with increase in temperature from 10-50 °C.[178]

The limited data available on surfactant solutions in ethylene glycol seem to show that in this polar solvent, as in water, the cmc decreases as the length of hydrophobic chain increases, but the change is much smaller than that in water.[179]

From the cmc data obtained in benzene and CCl_4 it has been concluded that (i) for the polyoxyethylenated nonionics, cmc's appear to decrease with increase in the length of the polyoxyethyelene group at constant hydrophobic chain length, and (ii) for the alkylaminium carboxylates listed, the cmc's in benzene appear to increase with increase in the length of the alkyl chain of the anion but to decrease with increase in the length of the alkyl chain of cation; in CCl_4, there is no significant change in the value of the cmc with these structural changes.[16,17,180-182]

The cmc is lower in D_2O than H_2O for different surfactants.[117,183] The hydrophobic bonds are expected to be stronger in D_2O than H_2O.[184] Micelles in D_2O are larger than H_2O.[185] The sudy of the effect of cosolvents on micelle formation in aqueous solutions is relatively new. It has originally been treated by Ray and Nemethy[166,186] and it has been reviewed later by Magid.[187] The formation of micelles in non aqueous polar solvents and in aqueous solutions containing cosolvents is of interest because it may result in a better understanding and practical applications of the process of micellization. In addition, some of the solvents such as ethylene glycol and glycerol have been widely used in protein conformation studies. The kind of interactions occurring in the formation of the micelles in polar solvents other than water are called solvophobic. The understanding of solvophobic interactions and micellization in non-aqueous and mixed aqueous media is considerably more nebulous.[188] The driving force for the micellization in such systems is less than that for water. The presence of the –OH group as

part of the structure of the solvent is not an absolute prerequisite for the presence of solvophobic interactions. In fact, micelles also form in solvents like formamide, and ethylene diamine. Surface tensiometric experiments indicated that DMSO increased the cmc of $C_{16}TAB$ in water at low concentrations.[189] A comparison between ethylene diamine, 2- aminoethanol and ethylene glycol shows that substitution of the –OH groups by $-NH_2$ groups gradually decreases the solvophobic effects.[166] This effect has been quantified per unit of $-CH_2-$ and is *ca.* – 2.89 kJ mol^{-1} for water, – 0.75 kJ mol^{-1} for glycerol and – 0.71 kJ mol^{-1} for ethylene glycol.[166,188,190,191] There seems to be no doubt that micellization is the result of a solvophobic effect and that this effect is not due to water alone, but many other solvents.

Aggregation Number

The number of surfactant molecules which aggregate to form micelle is called aggregation number (N) of that surfactant. It determines the size and geometry of the micelle and hence is an important parameter.

Aggregation numbers for surfactants in aqueous solution generally range between 10 and 100. Available methods for determining the number of monomers in the micelle include, light scattering, diffusion, viscosity and sedimentation velocity, ultrafilteration and nuclear magnetic resonance, and small-angle neutron scattering. Aggregation numbers are dependent on the nature and concentration of surfactant, the presence of inorganic/organic additives, the temperature, etc.[2,5,192-200]

In aqueous medium, the greater the dissimilarity between surfactant and solvent, the greater the aggregation number. Thus in aqueous solution, the aggregation number appears to increase with increase in the hydrophobic character of the surfactant.

Packing In Aqueous Assemblies

The surfactant packing parameter, also referred to as surfactant number, surfactant parameter, and critical packing parameter, is a dimensionless group relating the volume of the hydrophobic portion of a surfactant, v, the length of the hydrophobic portion of the surfactant, l, and the head group area, a_h. This group may be expressed as R_P where

$$R_P = v/a_h l \tag{1.4}$$

v and l are found from Tanford's formula[2]

$$l = 1.5 + 1.26n' \text{ Å} \tag{1.5}$$

$$v = 27.4 + 26.9\ n' \text{ Å}^3 \tag{1.6}$$

where n' is one less than the number of carbon atoms in the chain. Of course, v for a double-chain surfactant is twice that of a single-chain surfactant with the same length tail. Estimating headgroup areas is less straightforward since this parameter is very dependent on counterion adsorption and ionic strength. Counterion adsorption greatly modifies intermolecular headgroup repulsion, and this repulsion, greatly affects a_h. Similarly, ionic strength affects counterion adsorption as well as the shielding of intermolecular repulsion between the headgroups.

The following rules have been derived for predicting the dependence of structure on the surfactant packing parameter.[201,202]

$v/a_h l$	aggregate shape
<1/3	spherical micelles
1/3 to 1/2	rod-shaped micelles
1/2 to 1	vesicles or bilayers, 3-component o/w and biocontinious microemulsions
> 1	reverse micelles, w/o microemulsions.

These shapes may be related to assembly structural types with characteristic curvatures (Fig. 1.5).

Thermodynamics of Dilute Solutions of Surfactants

The driving forces for micellar aggregation primarily involve attractive and repulsive forces between the hydrophobic portions of surfactants and the net decrease in free energy obtained when these same hydrophobic portions no longer interact closely with water or other polar solvents. This kind of aggregation is similar to that found in the formation of dimers or trimers in solution, but the extent of aggregation during micellization is typically on the order of 10 to 100 monomers per micelle. While stepwise aggregation is a quantitatively useful way to keep track of such aggregation, it is also useful to think of micellization in terms of the so-called *pseudo*-phase approximation. In this approach micellization is likened to a phase transition, where the aqueous continuous part of the solution is considered one phase, and the micellar core or micelle itself is viewed as a second phase. Both approaches lead to equivalent results thermodynamically. A useful starting point for discussing micellization thermodynamics is to recapitulate a basic tenet of equilibrium systems, specifically that the chemical potential, μ, of a surfactant monomer in different states of aggregation is uniform.

A dilute solution of surfactant molecules can be considered to consist of solvent alongwith monomers, dimers, trimers, etc., and larger allowed aggregates (micelles, vesicles, liposomes, etc). Let us assume the concentration is so low that aggregates are considered to be non-interacting. The distribution of aggregates is then determined by the law of mass action,

$$\mu^{\circ}_{N} + (kT/N)\, ln\, (X_N / N) = \mu^{\circ}_{1} + kT\, ln\, X_1 \qquad (1.7)$$

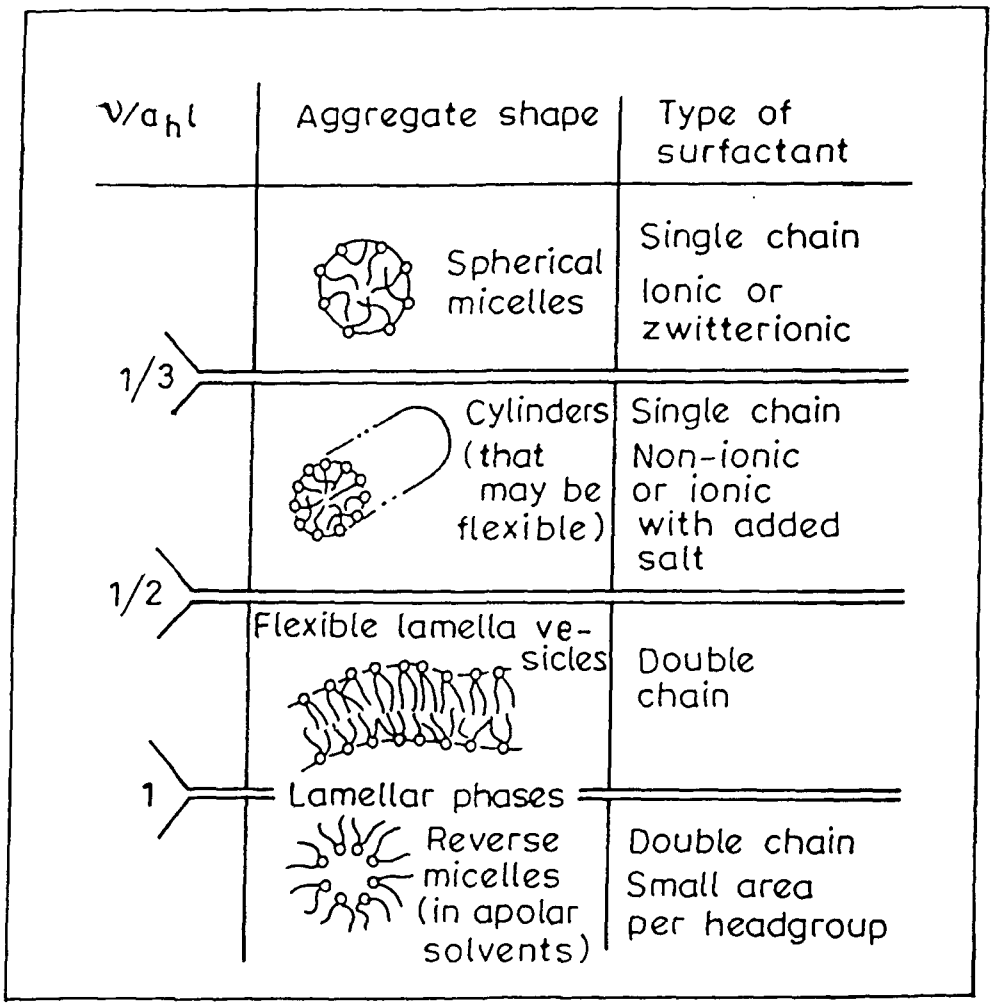


Fig. 1.5. Schematic diagram of possible aggregates shapes according to the $v/a_h l$ criterion.

where k is the Boltzmann's constant, T is temperature, and the suffix 1 denotes isolated amphiphiles. The chemical potential of an aggregate of size N has been written as $N\mu^{\circ}_N + kT\ ln\ (X_N/N)$. Implicit in Eq. (1.7) is the understanding that for any N a shape of minimum energy exists and is overwhelmingly more probable than its fellows.

Eq. (1.7) can be rewritten in the form

$$X_N/N = X_1^N \exp [N (\mu^{\circ}_1 - \mu^{\circ}_N) / kT] \qquad (1.8)$$

All aggregates can occur at any concentration, albeit with infinitesimal probability even below the cmc. Above the cmc, defined by $X_1 = \sum_{N-1}^{\infty} X_N$, X_1 increases slowly with concentration. It is shown[203] that if μ°_N is sharply distributed about some N then the distribution of aggregates peaks at a value of N just less than the N with minimum μ°_N and is also sharply distributed. Otherwise pronounced polydispersity may occur (e.g., for long, cylindrical micelles).

The entropic term $(kT/N)ln(X_N/N)$ in Eq. (1.7) has considerable nuisance value so it is helpful in dealing with finite aggregates to adopt a simpler basis for subsequent development. This is the so-called *pseudo*-phase approximation wherein the entropic term is dropped. In the *pseudo*-phase approximation no micelles occur below the cmc. (This is now the value X_1 of monomer concentration for which $\mu^{\circ}_N = \mu^{\circ}_1 + kT\ lnX_1$). Above this cmc all additional surfactant molecules form micelles or whatever aggregate has the minimum μ°_N. No other aggregates form until activity coefficients, i.e., interactions between aggregates, become significant. Keeping in view possible complications due to phase transitions and interactions the strategy is then to compare the chemical potentials of different aggregates to see which has the minimum μ°_N.

The form of μ°_N

The simplest version of current theory[203] assumes a form

$$\mu^{\circ}_N = \mu^{B}_N + \mu^{S}_N + \mu^{C}_N + \text{“ packing term”} \qquad (1.9)$$

= “bulk term” + “surface term” + “curvature term” + “packing term”

Bulk term : This is a constant term, the same for all aggregates, which measures the hydrophobic free energy of removing hydrocarbon tails from water into an assumed oil-like phase made up of all tails which form the micelle interior. The interior is assumed to be fluid in estimating this free energy transfer.

Surface term : This includes a term γ a to allow for the fact that hydrophobic tails still have some contact with water, where a is the area per surfactant molecule, and γ is the interfacial tension. Opposing this attractive energy is a term to account for repulsive headgroup interactions. These interactions can be due to steric repulsion, hydration, electrostatic, and other forces. If electrostatic in origin the simplest phenomenological description would give a term proportional to 1/a. The total surface contribution would then be written as

$$\mu^{S}_N = \gamma(a + a_h^2/a) \qquad (1.10)$$

which takes its minimum value $2\gamma a_h$ at an optimal area a_h per headgroup. This form for the repulsive contributions to μ^{S}_N cannot be taken literally, and its precise form is immaterial. Any mathematical description of the surface contributions which recognizes that several competing forces will lead to an optimal area a_h per headgroup will lead to the same conclusions.

Curvature term : If as an aid to analysing data on ionic micellar solutions we were to persist with an electrostatic model for headgroup repulsions,[203]

then for a curved, rather than planar, surface the term a in $\gamma a_h^2/a$ would be replaced by a(1+D/R) where R is the mean radius of curvature and D the Debye length. An alternative way of visualising a mechanism for curvature effects is to imagine that the centre of action for headgroup repulsion is displaced a distance D from the oil-water interface. Then a would be replaced by a $(1+D/R)^2$. The first form was chosen to have some plausible mathematical realization of the undoubted existence of curvature energy.

Packing term : The assumption that the interior of an aggregate is fluid-like and is to a first approximation incompressible has an immediate consequence, provided it is admitted that aggregates can obtain no holes. (The occurrence of an interior vacuum of water-filled region inside the (oil-like) interior of an aggregate would result in a large unfavorable increase in free energy, which possibility is excluded from consideration). This can be taken into account if we assume $\mu^\circ_N = \infty$, hence a packing criterion is violated. For spherical and cylindrical micelles this criterion is extreme, albeit useful, oversimplification. The melding of the two notions, of a fluid-like interior for the micelle and of packing, is at first sight contradictory. However, the two notions can be shown to be compatible in a first order theory.[204] Different possible candidates for aggregates (for water-surfactant system : spherical micelles, non-spherical micelles, vesicles, liposomes, bilayers and for oil-surfactant-water system : spherical drops, normal or inverted structures) were examined by Mitchell and Ninham and overall predictions were worked out. In addition to the contributions above to μ°_N there will be others with increasing concentration due to interactions.

Factors Affecting Structural Transitions

Amphiphilic molecules in aqueous solutions are known to form various types of micelles depending on the particular experimental

conditions. Usually, ionic amphiphilies form small globular micelles in binary solutions at low concentration near the cmc. Deviations from these simple initial conditions sometimes result in a strong modification of the size and shape of the micelles in solution; this is indicated by spectacular changes in some macroscopic properties of the solution such as turbidity and viscosity.

Actually this shape and size transition for the micelles can be achieved in various ways such as the following :

(1) a large increase of the amphiphile concentration[205]

(2) the addition of large amounts of certain mineral salts[18,206-216]

(3) the use of some organic additives (short-chained alcohols,[217,218] benzene, salicylate salts,[219] etc.).

At low surfactant concentrations, the micelles are usually spherical and the radius of the micelle is nearly equal to the length of the surfactant molecule. Upon increasing the concentration of surfactant, spherical micelles become cylindrical and subsequently the cylindrical structures become hexagonally packed. If concentration is further increased, the lamellar structures are formed. Further increase in concentration results in a hexagonal packing of water cylinders. Upon addition of oil and a short chain alcohol, one can convert such water cylinders into a water-in-oil microemulsion. The structures of these systems are well established from x-ray diffraction studies. It is possible to induce a transition from one structure to another by changing the physicochemical conditions such as temperature, pH, addition of salts, etc.

The addition of salts to aqueous surfactant solutions may result in a modification of both intermicellar and intramicellar interactions.

Consequently, solution properties, such as the critical micellar concentration, as well as the phase behavior of the surfactant solution, may be modified significantly upon the addition of salts.

The size, shape, polydispersity, and flexibility of ionic micelles are very sensitive to the presence of relatively high concentrations of electrolytes.[220-227] At lower salt concentrations only spherical micelles are formed, while at salt concentrations higher than threshold, larger rod like micelles are formed in equilibrium with the spherical micelles. There are at least two factors responsible for determining sphere to rod transition of micelle shape. One is the electrostatic effect of simple salt due to the counterion binding on ionic micelles, and the other is the hydrophobic interaction between surfactant molecules or ions caused by the change in the hydrogen-bonded structure of water.

Generally, the micelle aggregation number of a surfactant increases with increasing salt concentration, irrespective of whether the micelle is spherical or rodlike, and, above a certain threshold salt concentration, surfactant micelles exist as two forms, i.e., spherical and rodlike, that are in mutual equilibrium. Micellar growth has been observed by light scattering,[209,212,215,228] viscosity,[229-233] flow birefringence measurements,[220] and many other methods.

The effects of inorganic salts on ionic surfactant solutions have been discussed in terms of electrostatic interactions, ionic hydratability, changes in the water structure, etc., and have classified ions as water structure breakers and promoters.[30,234-238]

In contrast to inorganic cations, quaternary ammonium ions (R_4N^+) are essentially non-hydrated. The effect of the addition of quaternary ammonium

bromides, R_4NBr (R = H, CH_3 or C_4H_9), on the growth of SDS micelles has been studied by SANS measurements at 30 °C.[239] SDS form ellipsoidal micelles at 0.3 M concentration. At higher [R_4NBr], micellar growth is substantial in the case of tetra-*n*-butyl salt which is explained in the light of an increase in the Mitchell-Ninham parameter of the surfactant monomer.

Sein *et al.*[240] studied the effect of alkali metal and tetraalkylammonium chlorides on the dilute aqueous solution of sodiun dodecylbenzene-sulfonate. In this study addition of salts causes micelles to transform into lameller aggregates.

Swanson *et al.*[241] investigated the changes in size and microstructure of alkyltrimethylammonium halide (C_nTAX) micelles as a function of alkyl chain length and NaCl concentration in aqueous mixtures with and without trihydroxy or dihydroxy bile salts, sodium cholate (NaC) or sodiumdeoxycholate (NaDOC), have been investigated by *cryo*-TEM, time-resolved fluorescence quenching, and relative viscosity measurements. Without additions, dilute solutions of all the surfactants form globular micelles, with aggregation numbers increasing with the chain length. Addition of NaCl results in a growth of the micelles. For $C_{16}TA^+$ a transition to long threadlike micelles occurred in 2 M NaCl, whereas the micelles remain globular at shorter chain lengths. For $C_{18}TA^+$ a mixture of globular micelles and large structures was observed at 0.5 and 1.0 M NaCl. On addition of NaC to $C_{12}TA^+$, and $C_{14}TA^+$, in the presence of salt, a monotonous decrease in aggregation numbers with increasing concentration of NaC is found.

For the longer alkyl chains, a micellar growth resulting in a transition to threadlike cylindrical micelles occurs first, giving a peak in the viscosity. Further addition of NaC give smaller micelles.

When organic additives are added to aqueous micellar solutions, they are solubilized into the supramolecular assemblies and sometimes modify the assembly structures.

Investigations by Yiv *et al.*[242] and Leung and Shah[243] showed that short chain alcohols (C_1 to C_5) labilize SDS micelles, which was explained on the basis of the Aniansson and Wall theory[26] whereas short and medium chain length alcohols may lead to decrease in the micellar size,[244-248] addition of medium to long chain alcohols increase the aggregation number producing larger alcohol-surfactant mixed micelles.[244, 249-257]

These changes in micellar size are often explained in terms of differences in the solubilization mechanism of the alcohols. The principal location of alcohol molecules in aqueous micellar solution depends on the solubilizate itself.

While short chain length alcohols mainly affect the micelles through their effect on the solvent,[257-259] the medium chain length alcohols (butanol to hexanol) have distribution coefficients in the range 0.3 to 0.9 giving rise to mixed alcohol – surfactant aggregates.[244-247,249-266]

At high alcohol contents it has been proposed that the medium chain length alcohols are solubilized in the micellar interior as well as in the palisade layer, thus producing large alcohol swollen aggregates.[247,250-256]

Amines are more surface active than alcohols at the air-water interface.[267] Also, C_4 to C_{10} alkylamines have been found to be solubilized in SDS and CTAB micelles by electrostatic and hydrophobic effects, and the amine group is left on the surface of the micelle.[268] Aliphatic amines, which may exist in protonated form, have been found to be more effective with anionic surfactants.[269-272]

Kabir-ud-Din and his coworkers have shown that, like *n*-alcohols,[273,274] and *n*-amines,[273,275,276] aromatic hydrocarbons[277] are also potential candidates for such structural changes. These additives can be used to tune different intra- and intermicellar forces – van der Waals, hydrophobic, screened electrostatic,[192,278,279] etc. and effective Mitchell-Ninham parameter of the surfactant.

The aggregation number of the surfactant is observed to increase dramatically upon addition of higher alkanes such as octane, heptane or hexane. This can be due to the fact that these alkanes enter mainly the hydrophobic core. A small amount of octane can change the aggregation number as this addition can produce hydrophobic droplet in ionic micelles. It is observed that alkanes increase the micellar size.[280,281]

The solubilization of phenol and benzene in aqueous C_{12}TAB causes the micelle to swell, and it was observed that phenol addition leads to a greater increase in the size of aggregates than addition of benzene.[282] Ultraviolet absorbance measurements revealed that the site of solubilization within the micelles is different for the two additives: benzene solubilizes in the central core, while at low concentrations phenol is taken up in the outer palisade layer. However, the site of phenol solubilization, the shape of the micelles, and the physical properties of C_{12}TAB/phenol solutions change at a concentration of 1 mol of phenol solubilizate per mole of surfactant. Added electrolytes and organic additives are generally found to facilitate the transition, but Missel *et al.*[283] found that urea retards the transition of SDS in 0.8 M sodium chloride. In an extensive phase study, Guerin and Bellocq[284] have shown that various phases and critical points are present in the system sodium dodecyl sulfate (SDS/*n*-pentanol (C_5OH)/water/NaCl, depending on NaCl concentration and temperature. Low values of the mean aggregation

number (N) of SDS in aqueous solution of C_5OH have been found in several studies.[198,247,285] However, the addition of 0.1 M NaCl to solutions of SDS in pure water and to aqueous 0.2 M SDS + 0.6 M C_5OH increases N from 63 to 93[285,286] and from 47 to 197,[198] respectively. Thus, a larger increase of N is observed in SDS + C_5OH 'mixed micelles' upon addition of 0.1 M NaCl compared to pure aqueous SDS solution.

Recently, Kabir-ud-Din and coworkers[273,287-291] reported a kind of 'synergism' (e.g., significant increase in viscosity) in micellar systems when salts and organic additives are present concurrently in micellar solutions. In these studies the nature of salts and additives was found to play a crucial role towards such synergisms. The viscosity increase is explained in terms of micellar growth and the decrease in terms of swollen micelle formation (due to interior solubilization of organic additive) or micellar disintegration (due to the formation of water + additive *pseudo*-phase). With cetylpyridinium bromide (CPB), an opposite viscosity behavior to that of simple inorganic salts was found when aromatic hydrocarbons were added in the presence of tetra-*n*-butylammonium bromide (Bu_4NBr); it is obvious that with CPB, Bu_4N^+ would behave as co-ion and would remain in the bulk solvent to affect the micellar structure (by changing the solubilization site of aromatic hydrocabrons).[289]

Clouding Phenomenon in Aqueous Surfactant Solutions

The stabilities of surfactant solutions with respect to temperature need to be known, especially where elevated temperature prevails.[292,293] Nonionic surfactant solutions posses a complex phase behavior[78,294] including partial miscibility, where above a critical temperature (the cloud point) the system spontaneously separates into two distinct phases. One surfactant-rich and the

other water-rich. The absence of long range electrostatic interactions between aggregates and the decreasing hydration of nonionic headgroups with increasing temperature result in the spontaneous phase separation (lower consolute boundary). Classically, below a lower consolute boundary (LCB) two components (surfactant and water) are completely miscible while above the boundary the two components become partially miscible and form two separate phases. On the other side, an upper consolute boundary (UCB) separates a low-temperature region in which the two components are only partially miscible and form two phases from a high–temperature region in which both components are completely miscible.

The clouding behavior in surfactant solutions is well documented in two situations: nonionic surfactants in water[293,295,296] and cationic surfactants in concentrated aqueous salt solutions.[297,298] However, former class of surfactants has been investigated in far greater details than the ionic ones.

The microscopic origins of phase separation are still elusive. In the literature[152.217.299-305] there has been a long dispute as to whether the phase separation, observed as a cloud point, is connected with a rapid increase in micellar size at an increased temperature or with as aggregation of relatively small micelles. Another possibility is an aggregation of large micelles. Turbidity measurements[152.299.301.303] have been performed in order to determine the micellar size. The standard interpretation of these results is that the micellar aggregation number increases very rapidly when the CP is approached. This interpretation has been criticized[300,305] because the turbidity must show a big increase owing to the presence of the CP, a

phenomenon that has nothing to do with an increase in the molecular weight of the micelles.

Scattering investigations manifest a strong low-angle component in both kinds of solution exhibiting lower consolute temperatures.[306] Historically this was ascribed to micelle growth with increasing temperature but is now widely associated with attractions between micelles. The existence of attractive interactions between polyoxyethylenealkyl ethers at elevated temperatures has been demonstrated convincingly by Claesson *et al.*[307] Changes in the hydration of the hydrophilic ethylene oxide moieties of nonionic surfactants with temperature is widely viewed as the cause of phase separation. This approach differs from the direct H-bond approach associated with hydration models. Rather it presents a change in the nature of the solute molecule with temperature.

Kjellander[308.309] has argued persuasively that attractions between spherical micelles cannot give rise to the low observed critical concentrations but are a consequence of attractions between anisotropic micelles. He also showed that micelle growth alone is insufficient to cause phase separation. Lindman[310] has advanced a model based on conformational changes in the polyoxyethylene chain with changing temperature, from which a change in the dipole moment of the hydrophilic chain arises. This in turn leads to a decrease in the polarity or hydrophilicity of the surfactant and hence to phase separation. In ionic surfactant-electrolyte solutions little is known about the attractive potential. Porte[297,298] has suggested an analogy with the Flory-Huggins phase separation of polymers in a poor solvent, based largely on the wormlike structure of ionic micelles at high ionic strength.

RELEVANCE

The number of scientific reports relating to amphiphilic molecules (e.g., surfactants) has greatly expanded during the past 3-4 decades. Surfactant molecules are not only highly interesting from the physicochemical view point but also similar to molecules fundamental to life (e.g., lipids, proteins, etc.): it is no exaggeration to say that living things are made up of aggregates comprising wide variety of amphiphiles. Therefore, a considerable amount of research work has been directed towards determining the physicochemical properties of self-assembled surfactant aggregates, especially micelles. Although many reasons can be cited for the widespread interest in elucidating the physicochemical properties of micelles, there are primarily three reasons. Firstly, one can consistently and easily prepare aqueous micellar solutions which have aggregates of colloidal dimensions with characteristic size, shape, and surface properties. Hence these systems have been employed as model systems in investigations concerned with understanding colloidal physicochemical phenomenon. Secondly, the similarities between surfactant aggregates and biological lipid membranes have not gone unnoticed. Thus, in many studies micelle-like aggregates have served as rudimentary model systems for biological lipid membrane systems. Thirdly, it has been found that micelles can act as unique reaction media. Indeed, solubilization of reactants within self-assembled surfactant aggregates frequently leads to altered reaction rates, reaction routes, and stereochemistries. Obviously, micelles cannot be fully exploited as reaction media until physicochemical properties have been ascertained. The factors involved in localizing different species within the interfacial microenvironment of surfactant aggregates can assist researchers in interpreting some of the hitherto

enigmatical biological processes which take place in the analogous interfacial microenvironments.

Most of the applications of the surfactants are related to their state of aggregation. The aggregation process depends, of course, on the amphiphilic species and solvent conditions in which they are dissolved. Therefore, study of aggregation of surfactants under a variety of solution conditions has significance – both from basic and applied view points.

Lay out of the Thesis

In surfactant applications salts and/or organic additives are required to be present simultaneously. Therefore, a fundamental understanding of how salts affect the micellization and related phenomenon in aqueous surfactant solutions may lead to an effective utilization of such systems for various practical purposes as, even now, most utilization of surfactants are based on their micellization behavior (singly or with other additives). Also, presence of salts in aqueous surfactant solutions may result in a modification of both intramicellar and intermicellar interactions. It is, therefore, of genuine chemical interest to ascertain the effect of the combined presence of salts and organic additives on the aggregation phenomenon. Hence an up-to-date literature survey related to the topic is included in **Chapter-I**. From the survey it appears that influence of inorganic salts on micellization is well documented but with quaternary salts the situation is not the same and only a few reports are available.

Chapter–II includes methodologies, the list of chemicals used, their formulas, make and % purity. **Chapter–III** describes the study of micellization of SDBS in presence of inorganic and quaternary salts.

Micellar growth/dissociation has been influenced by organic additives and salts. **Chapter–IV** is, therefore, devoted to viscometric studies on micellar growth and solubilization sites wherein the influence of the presence of quaternary bromides on the change in solubilization site of organic compounds in cationic micellar solutions (C_{16}TAB and C_{14}TAB) has been described.

Similar viscometric studies were performed with aqueous SDBS in presence of cyclic organic compounds and aniline which are detailed in **Chapter-V**. **Chapter-VI** includes small-angle neutron scattering (SANS) studies on a system (SDBS + tetra-*n*-butylammonium bromide) which shows clouding under certain concentration and temperature ranges. The SANS data under the LCB and above UCB of the system were collected and analyzed.

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CHAPTER II

EXPERIMENTAL

The chemicals used throughout the study are listed in Table 2.1, alongwith their abbreviated names, chemical formulas, sources and purities.

Due to their hygroscopic nature the quaternary salts were stored in a desiccator over P_2O_5. All the salts and additives were used as received.

Preparation of Solutions

The water used to prepare the solutions was demineralized and double-distilled in all glass (Pyrex) distillation apparatus. The specific conductivity of the water was in the range of 1-2 x 10^{-6} S cm^{-1}. D_2O of 99.4% purity, for the small-angle neutron scattering experiments, was supplied by the heavy water division, Bhabha Atomic Research Centre (BARC), Mumbai.

Special care was taken for cleaning the glasswares. The glasswares were properly washed with freshly prepared chromic acid and distilled water then rinsed with acetone and kept in oven for drying before use.

Stock solutions of surfactants (in water containing either a fixed concentration of salt or no salt) were prepared volumetrically. The sample solutions were made by taking the required volumes of the additives with the help of microliter syringes (Hamilton) in standard volumetric flasks and making up the volumes with the stock solution. The error chances in composition of the samples were not more than ± 0.02%. After proper mixing, the sample solutions were kept overnight for equilibration. Prior to measurements, these solutions were kept at the desired temperature for at least 1 hr to attain thermal equilibrium. To avoid evaporation, the flasks/ viscometer were kept properly stoppered and sealed during equilibration.

The temperature was controlled within ± 0.1 °C in a thermostatic water bath which was designed and assembled in the laboratory with commercially available components.

TABLE - 2.1.

Names and Structural Formulas of the Chemicals Used.

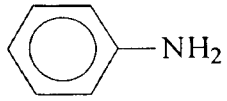
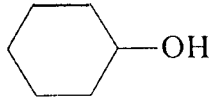
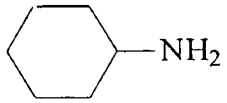
Name	Abbreviation	Structure/Formula	Make	% purity
a. Surfactants				
Cetyltrimethylammonium bromide	CTAB or C_{16}TAB	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$	Sigma (St. Louis)	99
Tetradecyltrimethylammonium bromide	TTAB or C_{14}TAB	$CH_3(CH_2)_{13}N^+(CH_3)_3\ Br^-$	Sigma (St. Louis)	99
Sodium dodeylbenzene sulfonate	SDBS	$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$	TCI (Japan)	$\geq$ 99
b. Quaternary Salts				
Tetramethylammonium bromide	Me_4NBr	$(CH_3)_4NBr$	Fluka (Switzerland)	$\geq$ 97
Tetraethylammonium bromide	Et_4NBr	$(C_2H_5)_4NBr$	Fluka (Switzerland)	$\geq$ 98
Tetra-*n*-propylammonium bromide	Pr_4NBr	$(C_3H_7)_4NBr$	Fluka (Switzerland)	$\geq$ 98
Tetra-*n*-butylammonium bromide	Bu_4NBr	$(C_4H_9)_4NBr$	Fluka (Switzerland)	$\geq$ 98
Tetra-*n*-pentylammonium bromide	Am_4NBr	$(C_5H_{11})_4NBr$	Fluka (Switzerland)	$\geq$ 99
Tetra-*n*-octylammonium bromide	Oc_4NBr	$(C_8H_{17})_4NBr$	Fluka (Switzerland)	$\geq$ 98
Tetra-*n*-butylphosphonium bromide	Bu_4PBr	$(C_4H_9)_4PBr$	Fluka (Switzerland)	$\geq$ 98
Tetraphenylphosphonium bromide	ϕ_4PBr	$(C_6H_5)_4PBr$	Lancaster (England)	98+
n-propyltriphenylphosphonium bromide	$Pr\phi_3PBr$	$C_3H_7(C_6H_5)_3PBr$	Lancaster (English)	99

contd.....

c. Inorganic Salts

Lithium bromide		LiBr	Riedel-de-Haen (Germany)	99.4
Potassium bromide		KBr	Merck (India)	99
Sodium bromide		NaBr	Lobachemie (India)	99
Ammonium bromide		NH_4Br	Merck (India)	99

d. Additives

n-Heptane		$CH_3(CH_2)_5CH_3$	Qualigens (India)	95
n-Heptanol	C_7OH	$CH_3(CH_2)_5CH_2OH$	BDH (England)	99
n-Heptylamine	C_7NH_2	$CH_3(CH_2)_5CH_2NH_2$	Fluka (Switzerland)	> 98
Aniline			Merck (India)	99
Cyclohexane			BDH (India)	95
Cyclohexanol			BDH (India)	95
Cyclohexylamine			BDH (England)	99.75

As the studies described in the thesis involve conductivity, viscosity, cloud point and SANS measurements of the sample solutions, brief descriptions of the techniques are given in the following pages.

Conductivity Measurements

The electrical conductivity of aqueous solutions of surfactants with or without salts (quaternary ammonium, phosphonium and inorganic) were measured with ELICO conductivity bridge (type CM 82T) using platinized electrodes with the cell constant 1.02 cm^{-1}. Aqueous surfactant solutions were prepared by successive dilutions of a concentrated sample. Critical micelle concentrations (cmc) were derived from the break points in the specific conductivity *vs.* concentration curves. The conductivity can be linearly correlated to the [surfactant] in both the pre-micellar and post-micellar regions and the ratio of the slopes gives the degree of counterion dissociation (α).

Viscosity Measurements

Viscosity is the measure of internal friction of a fluid, caused by molecular attraction, which makes it resist a tendency to flow. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required to cause this movement which is called *shear*. Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading, spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less viscous materials. Newton defined viscosity as

$$F/A = \eta.dv/dx \qquad (2.1)$$

The term F/A indicates the force per unit area required to produce the shearing action. It is referred to as *shear stress* and is symbolized by F'. Its

unit of measurement is 'dynes per square centimeter' (dynes/cm^2). The velocity gradient, dv/dx, is a measure of the speed at which the intermediate layers move with respect to each other. It describes the shearing the liquid experiences and is thus called *shear rate*. Its unit of measure is called the 'reciprocal second'. η is a constant for a given material and is called its *viscosity*.

Using the simplified terms, viscosity may be defined mathematically by the formula :

$$\eta = \text{viscosity} = F'/s = \text{Shear stress /shear Rate} \qquad (2.2)$$

The fundamental unit of viscosity measurement is the 'poise'.

Fluids have different rheological characteristics that can be described by viscometric measurements. There are two categories of fluids.

Newtonian : These fluids have the same viscosity at different shear rates and are called Newtonian over the shear rate range they are measured.

Non-Newtonian : These fluids have different viscosities at different shear rates. They fall into two groups:

1. Time independent non-Newtonian
2. Time dependent non-Newtonian.

The time dependency is the time they are held at a given shear rate.

Viscometry : Liquids exhibit much greater resistance to flow than gases, and consequently they have much higher viscosity coefficients. The viscosity coefficients of gases increase with temperature, while just the reverse is generally true of liquids; the viscosity of most liquids decreasing with rising temperature.

The viscosity coefficients for gases at moderate pressures are essentially independent of pressure, while increase of pressure leads to an increase in viscosity for liquids.

The measurements of the viscosity of liquids are based on either the Poiseuille or Stokes equations. Poiseuille, in 1842, proposed the following equation for the coefficient of viscosity of a fluid.

$$\eta = \pi P r_4 t / 8lV \qquad (2.3)$$

Here V is the volume of liquid of viscosity η which flows in time t through a capillary tube of radius r and length *l* under a pressure head of P dynes per square centimeter. If we measure the time of flow of the same volume of two different liquids through the same capillary, then, according to Poiseuille equation, the ratio of the viscosity coefficient of the two liquids is given by

$$\eta_1 / \eta_2 = P_1 t_1 / P_2 t_2 \qquad (2.4)$$

Since the pressures P_1 and P_2 are proportional to the densities of the two liquids ρ_1 and ρ_2, then

$$\eta_1 / \eta_2 = P_1 t_1 / P_2 t_2 = \rho_1 t_1 / \rho_2 t_2 \qquad (2.5)$$

Consequently, once ρ_1, ρ_2 and η_2 are known, determination of t_1 and t_2 permits the calculation of η_1, the viscosity coefficient of the liquid under consideration. In the present investigations, the viscosities of the solutions were measured by an Ubbelohde viscometer thermostated at desired temperatures (± 0.1 °C).

At higher additive concentrations, the viscosities were dependent on the rate of flow. Therefore, to obtain viscosities under Newtonian flow

conditions, a wide U-shaped tube containing water was connected to the limb of the viscometer.[1] This arrangement allowed us to vary the pressure (P) under which the solution flows and thus to determine viscosity values at various rates of flow (at least four flow time measurements were made at each cocentration/rate of flow, and mean deviation from the mean of all measurements not exceeding 0.1 s was required) from the slope of straight line obtained by variation of P *vs.* 1/t (according to the equation $P = \eta A/t$, where A is the characteristic constant of the viscometer obtained by calibration with liquids of known viscosities). The relative viscosity of the solution , $\eta_r = \eta/\eta_o$ (where η_o is the viscosity of the solvent water), is given by $\eta/\eta_o = \rho t/\rho_o t_o$, where ρ and ρ_o are the densities of the solution and water and t_o is the flow time of water. At a surfactant concentration C, ρ is given by

$$\rho = \rho_o + (1+\bar{V}\rho_o)C \qquad (2.6)$$

($\bar{V}$ is the partial specific volume of the surfactant). It has been reported that variation in ρ was insignificant when either the surfactant or additive concentrations were varied. Therefore, density corrections were not made[2] and η_r values were calculated using equation,

$$\eta_r = t/t_o \qquad (2.7)$$

CP Measurements

For CP measurements, samples were prepared in distilled water by taking requisite amounts of SDBS and tetra-*n*-butylammonium bromide in graduated Pyrex glass tubes. The tubes were stoppered and then placed in a temperature-controlled water bath (stability ± 0.1 °C). The temperature was slowly raised until clouding appeared (LCST) and it was noted visually. When the temperature was further raised the solution became clear again (UCST).

Various such points obtained with different salt concentrations were used to construct lower and upper consolute boundaries (LCB and UCB).

Small-Angle Neutron Scattering : Technique and Measurements

Small-angle neutron scattering (SANS)[3-7] is a powerful technique for studying structural features of the inhomogeneities (particles) or the density fluctuations in condensed matter for a length scale ranging from one nanometer up to one micron. 'Structural features' include size or size distribution, shape, dimensionality, interparticle spatial correlation, etc. SANS is widely used to investigate the structure (shape and size) of different kinds of mesoscopic systems such as micellar solutions, magnetic fluids, protein solutions and colloidal suspensions. SANS is an elastic scattering process, which is related to scattering properties at small momentum transfer vector and is caused by the variation of scattering length density over a distance exceeding the normal inter-atomic distances in condensed systems. The consideration of scattering at low momentum transfer makes the SANS technique suitable to study gross-scale structural properties of a medium overlooking the specific details over inter-atomic distances.

SANS experiment is a diffraction experiment which involves scattering of a monochromatic beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle. The wave vector transfer, Q (= $4\pi\sin\theta/\lambda$, where λ is the incident neutron wavelength and 2θ is the scattering angle) in these experiments is small, typically in range of 10^{-3} to 1.0 $Å^{-1}$. The wavelength of neutrons used for these experiments being 4-10 Å, the smallest Q occurs at small scattering angles (~1°). The technique is, therefore, called small-angle neutron scattering.

The SANS spectrometer at Dhruva reactor, BARC, Mumbai, is a simplified version of the conventional machines (Fig. 2.1). A 10 cm dia neutron beam from the reactor is reduced to 1.5 x 1.0 cm^2 at the sample position by using an inpile collimator and two slits (entrance and exit) outside the biological shield. The collimator design and the apertures are chosen such that sample sees the angular divergence of ± 0.5°. The experiments use incident neutrons of mean wavelength 5.2 Å with sample-to-detector distance 1.85 m. Before reaching the sample, the beam from the reactor is allowed to pass through a 15 cm long polycrystalline BeO filter which is used as a monochromator. This monochromatic beam has a resolution ($\Delta\lambda/\lambda$) of about 15%. The incident neutron flux at sample position is 2.2 x 10^5 neutrons cm^{-2} s^{-1}. A 10 x 10 cm^2 sample table has been provided to mount the sample. The angular distribution of the beam is recorded with a 100 cm long, 3.8 cm dia He^3 linear position sensitive detector (PSD). The detector is housed in a massive shielding to reduce the background. The PSD is made up of a stainless steel tube filled with He^3 gas at 2.04 atm and Kr at 1.02 atm pressure.

Data from the position sensitive detector are stored in a multichannel analyzer as intensity *vs.* channel number. In a SANS experiment, in addition to recording the intensity distribution $I_s(Q)$ with the sample, one has to measure two types of backgrounds $I_b(Q)$ and $I_e(Q)$. The room background $I_b(Q)$ is measured by putting cadmium at the sample position. $I_e(Q)$ is the residual part of the direct beam and is measured without any sample in the beam or by having an empty sample holder at the sample position in case such a holder is used in the experiment. The measured intensity from the sample $I_s(Q)$ is corrected for these contributions. The corrected scattered intensity I(Q) of interest from the sample is given by[8]

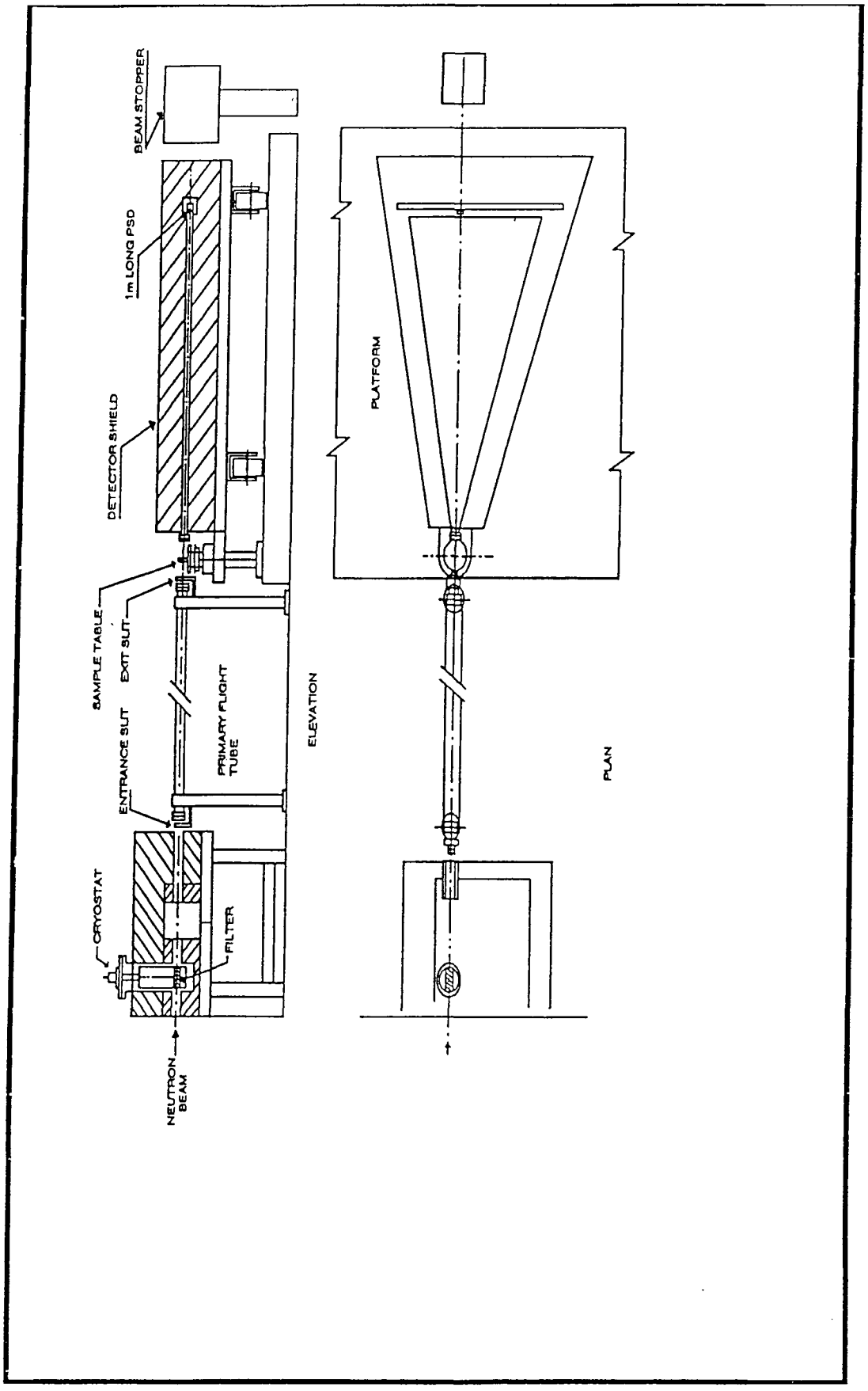


Fig. 2.1. Schematic of a SANS diffractometer.

$$I(Q) = \left[\frac{I_s(Q) - I_b(Q)}{T_s} - \frac{I_e(Q) - I_b(Q)}{T_e} \right] T_s \qquad (2.8)$$

where T_s is the sample transmission and T_e is the transmission of the empty sample holder. $I_s(Q)$, $I_b(Q)$ and $I_e(Q)$ in Eq. (2.8) correspond to identical monitor counts.

In a SANS experiment, the sample is usually taken in the form of a plate (circular or rectangular), so that it has uniform thickness over the beam area. If $d\Sigma/d\Omega(Q)$ is the differential scattering cross-section per unit volume of the sample, the measured scattered intensity is given by[9]

$$I(Q) = KT_s t \frac{d\Sigma}{d\Omega}(Q) \qquad (2.9)$$

where t is the sample thickness and K a constant which depends on instrumental parameters such as incident neutron flux, detector efficiency, solid angle subtended by detector element at sample position, etc.

By combining Eqs. (2.8) and (2.9), we get the following expression for the scattering cross-section of the sample :

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{1}{Kt}\left[\frac{I_s(Q) - I_b(Q)}{T_s} - \frac{I_e(Q) - I_b(Q)}{T_e} \right] \qquad (2.10)$$

The instrumental constant K is determined by recording the data from a standard sample (e.g., H_2O, vanadium, etc.).[9] The measurement thus provides $d\Sigma/d\Omega(Q)$ in absolute units, namely cm^{-1}.

Scattered neutron intensity in a SANS experiment depends on the square of the difference between the average scattering length densities of the particle and the solvent, $(\rho_p - \rho_m)^2$; this is referred to as contrast factor. SANS signal from micellar solutions increases many times when D_2O is used instead of H_2O. This is due to the fact that the scattering length of

hydrogen is negative (= – 0.3723 x 10^{-12} cm) and that for deuterium is positive (= 0.6674 x 10^{-12} cm). The contrast between the particle and the solvent can be increased by deuterating either the solvent or the particle. All samples were, therefore, prepared in D_2O. For measurements, the samples were held in a 0.5 cm pathlength quartz cell.

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CHAPTER III

EFFECT OF INORGANIC AND QUATERNARY BROMIDES ON THE MICELLIZATION OF SODIUM DODECYLBENZENESULFONATE IN AQUEOUS SOLUTIONS

INTRODUCTION

One of the most important features of surfactants is their ability to aggregate into micelles. The aggregation alters the characteristics of the solution, which is relevant for applications of surfactants in household, cosmetics, pharmaceuticals, etc. Also of great importance for the behavior of surfactant systems, such as micellization and micellar growth, are the interaction forces between and within the surfactant aggregates.

In many applications of surfactants, salts and/or organic additives are required to be present simultaneously. Accordingly, a fundamental understanding of how salts affect the micellization in aqueous surfactant solutions may lead to a more effective utilization of these systems in various practical applications as, even now, most utilization of surfactants are based on their micellization behavior (singly or with other additives). Presence of salts in aqueous surfactant solutions may also result in change of both intramicellar and intermicellar interactions. It is, therefore, of genuine chemical interest to ascertain the effect of the combined presence of electrolytes and other organic additives on the phenomenon of micellization and other related properties (aggregation number , degree of dissociation (α), etc.). Recently, a lot of work has been produced to understand the effect of various additives on the micellization as well as on the above interaction forces.[1-10]

Micelles with charged surfaces bind counterions selectively and their solution properties are sensitive to concentration and type of the counterion.[11,12] Also, the counterions perturb the local ordering or 'structure' of water molecules. Several water molecules are bound to counterions due to ion-dipole interaction.

Quaternary salts, which ionize like ordinary inorganic salts, also have organic moiety enabling them to interact hydrophobically with exposed hydrocarbon chains of surfactant monomers. In contrast to their alkali metal counterparts, these symmetrical quaternary ammonium ions (R_4N^+) are essentially nonhydrated. In aqueous solutions the R_4N^+ exhibit an ambivalent nature . In these ions the single positive charge is burried in a paraffin shell. The 'salting in' effects of these salts are in contrast to 'salting out' effects of the small inorganic salts. Since R_4N^+ cations modify the structure of water around them in a way similar to some simple hydrocarbons,[13] it could be of considerable interest to see how this interaction affects various related micellization parameters (cmc, α, micellar growth , viscosities of solutions, etc.).

Recently, ionic surfactants have been found to exhibit some unusal behavior in the presence of quaternary salts.[14,15] The present work was undertaken with conductivity measurements in sodium dodecylbenzene-sulfonate (SDBS), a commonly used surfactant for various commercial / technical applications.[12,16,17] The purpose of the present study was three-fold : (i) to study micellization behavior of SDBS in presence of simple inorganic and quaternary bromides; (ii) to see the simultaneous electrostatic and hydrophobic effects of salts on the cmc of SDBS; (iii) to compare the effect of quaternary vis-a-vis simple inorganic salts on the cmc of SDBS.

RESULTS

The specific conductivity of SDBS solutions in the absence and presence of salts (inorganic or quaternary) are given in Tables 3.1-3.9. The relevant conductivity *vs.* [SDBS] plots are shown in Figs. 3.1-3.9. The variation of cmc of SDBS in presence of inorganic and quaternary salts are

TABLE-3.1.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of lithium bromide in water at 25 °C.

C / mM	$\kappa \times 10^4$/S cm^{-1}			
	x → 0.0	4.0	6.0	8.0
0.06	-	-	-	12.81
0.12	-	5.12	8.81	13.43
0.19	-	-	-	13.73
0.25	1.85	5.73	9.62	14.44
0.31	-	-	-	15.06
0.37	-	6.95	10.65	15.54
0.43	-	-	-	16.08
0.49	-	7.77	11.47	16.38
0.55	-	-	-	16.79
0.61	-	8.38	12.38	17.30
0.67	-	-	-	17.71
0.73	5.24	9.20	12.99	18.10
0.79	-	-	-	18.52
0.84	-	10.12	13.71	19.04
0.90	-	-	-	19.65
0.96	6.86	10.73	14.52	19.95
1.02	-	-	-	20.46
1.07	-	11.75	15.24	20.77
1.13	-	-	-	21.18
1.19	8.44	12.46	16.46	21.69
1.24	-	-	-	21.99
1.30	-	-	16.77	22.60
1.35	-	-	-	22.80
1.38	-	13.28	-	-
1.41	10.16	14.09	17.99	23.52
1.47	-	-	-	24.10
1.52	10.87	14.60	18.81	24.54
1.58	-	-	-	24.64
1.63	11.48	15.62	19.62	24.95
1.68	-	-	-	25.56
1.74	12.30	16.75	20.24	25.77
1.79	-	-	-	26.17
1.85	12.81	17.46	21.15	26.68

Contd...

1.95	14.13	18.38	21.87	-
2.06	14.95	18.89	22.68	-
2.16	15.56	19.80	23.09	-
2.27	16.18	20.42	23.70	-
2.37	16.89	21.03	24.52	-
2.47	17.80	21.85	25.20	-
2.57	18.62	22.66	25.95	-
2.67	-	23.27	26.66	-
2.77	-	23.68	27.27	-
2.87	20.46	24.20	27.99	-
2.97	21.48	25.01	28.60	-
3.07	21.99	25.60	28.91	-
3.16	22.60	-	-	-
3.26	23.01	-	-	-
3.35	23.42	-	-	-
3.44	24.13	-	-	-
3.54	24.74	-	-	-
3.63	25.25	-	-	-
3.72	25.76	-	-	-
3.81	26.58	-	-	-
3.92	27.29	-	-	-
3.99	27.70	-	-	-
4.07	27.90	-	-	-
4.16	28.31	-	-	-
4.25	29.23	-	-	-
4.34	29.74	-	-	-
4.67	30.96	-	-	-
5.00	31.17	-	-	-

TABLE-3.2.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of sodium bromide in water at 25 °C.

C / mM	$\kappa \times 10^4$/S cm^{-1}			
	x → 0.0	4.0	6.0	8.0
0.06	-	-	-	12.81
0.12	-	4.82	9.32	13.43
0.18	-	-	-	13.73
0.25	1.85	5.73	10.34	14.44
0.31	-	-	-	15.06
0.37	-	6.75	11.36	15.57
0.43	-	-	-	16.08
0.49	3.55	7.47	12.28	16.38
0.55	-	-	-	16.79
0.61	-	8.38	13.10	17.30
0.67	-	-	-	17.71
0.73	5.24	9.10	13.91	18.10
0.79	-	-	-	18.52
0.84	-	10.22	14.52	19.04
0.90	-	-	-	19.65
0.96	6.86	11.24	15.34	19.95
1.02	-	-	-	20.46
1.07	-	11.95	16.46	20.77
1.13	-	-	-	21.18
1.19	8.44	12.87	17.18	21.69
1.25	-	-	-	21.99
1.30	-	13.48	18.09	22.60
1.35	-	-	-	22.80
1.41	10.15	14.20	18.91	23.52
1.47	-	-	-	24.10
1.52	10.87	14.71	19.62	24.54
1.58	-	-	-	24.64
1.63	11.48	16.03	20.24	24.95
1.68	-	-	-	25.56
1.74	12.30	16.54	20.95	25.77
1.79	-	-	-	26.17
1.85	12.81	16.95	21.66	26.68
1.95	14.13	17.97	22.38	-

Contd...

2.06	14.95	18.89	22.99	-
2.16	15.56	19.40	23.70	-
2.27	16.18	19.91	24.30	-
2.37	16.89	20.62	25.03	-
2.47	17.80	21.74	25.54	-
2.57	18.62	21.74	26.46	-
2.67	-	22.25	27.07	-
2.77	-	23.38	27.38	-
2.87	20.46	23.99	27.78	-
2.97	21.48	24.80	-	-
3.07	21.99	25.50	-	-
3.16	22.60	26.34	-	-
3.26	23.01	-	-	-
3.35	23.42	-	-	-
3.44	24.13	-	-	-
3.54	24.74	-	-	-
3.63	25.25	-	-	-
3.72	25.76	-	-	-
3.81	26.58	-	-	-
3.92	27.29	-	-	-
3.99	27.70	-	-	-
4.07	27.90	-	-	-
4.16	28.31	-	-	-
4.25	29.23	-	-	-
4.34	29.74	-	-	-
4.67	30.96	-	-	-
5.00	31.17	-	-	-

TABLE-3.3.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of ammonium bromide in water at 25 °C.

C/ mM	$\kappa \times 10^4$/S cm^{-1}			
	$x \rightarrow 0.0$	4.0	5.0	6.0
0.12	-	4.71	-	12.09
0.25	1.85	5.53	9.83	13.63
0.37	-	6.14	-	14.34
0.49	3.55	7.36	11.47	14.95
0.61	-	8.28	-	16.28
0.73	5.24	9.10	12.69	17.30
0.84	-	10.01	-	17.81
0.96	6.86	10.83	14.12	18.42
1.07	-	11.54	-	18.83
1.19	8.44	12.26	15.44	19.85
1.30	-	12.77	-	20.46
1.41	10.16	13.58	17.18	21.18
1.52	10.87	14.60	-	21.79
1.63	11.48	15.42	18.40	22.60
1.74	12.30	16.03	-	23.01
1.85	12.81	16.85	19.83	23.73
1.95	14.13	17.56	-	24.44
2.06	14.95	18.28	21.26	24.95
2.16	15.56	18.89	-	25.56
2.27	16.17	19.70	22.07	26.07
2.37	16.89	20.32	-	26.68
2.47	17.80	20.83	23.30	27.19
2.57	18.62	21.44	-	27.70
2.67	-	21.95	24.52	28.21
2.77	-	22.66	-	28.83
2.87	20.46	23.17	25.52	-
2.97	21.48	23.68	-	-
3.07	21.99	24.19	26.36	-
3.16	22.60	24.80	-	-
3.26	23.01	-	27.38	-
3.35	23.42	-	-	-
3.44	24.13	26.13	28.09	-
3.54	24.74	-	-	-

Contd...

3.63	25.25	-	28.60	-
3.72	25.76	-	-	-
3.81	26.58	-	-	-
3.92	27.29	-	-	-
3.99	27.70	-	-	-
4.07	27.90	-	-	-
4.16	28.31	-	-	-
4.25	29.23	-	-	-
4.34	29.74	-	-	-
4.67	30.96	-	-	-
5.00	31.17	-	-	-

TABLE-3.4.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of tetramethylammonium bromide in water at 25 °C.

C / mM	$\kappa \times 10^4$/S cm^{-1}					
	x → 0.0	0.4	1.0	2.0	4.0	6.0
0.06	-	-	9.12	-	-	-
0.12	-	5.38	9.83	12.92	17.32	21.83
0.18	-	-	10.45	-	-	-
0.24	-	-	11.06	-	-	-
0.25	1.85	6.82	-	14.65	18.85	23.06
0.30	-	-	11.67	-	-	-
0.36	-	-	12.18	-	-	-
0.37	-	8.25	-	16.08	20.18	23.98
0.42	-	-	12.79	-	-	-
0.48	-	-	13.61	-	-	-
0.49	-	9.17	-	17.50	21.40	25.20
0.54	-	-	14.32	-	-	-
0.59	-	-	14.83	-	-	-
0.61	-	11.26	-	18.83	22.53	26.63
0.65	-	-	15.44	-	-	-
0.71	-	-	16.26	-	-	-
0.73	5.24	12.81	-	19.95	23.95	27.85
0.76	-	-	16.87	-	-	-
0.82	-	-	17.18	-	-	-
0.84	-	13.81	-	21.18	24.67	28.67
0.87	-	-	17.48	-	-	-
0.95	-	-	18.09	-	-	-
0.96	6.86	15.14	-	22.60	25.89	30.09
0.98	-	-	18.71	-	-	-
1.03	-	-	19.22	-	-	-
1.07	-	16.36	-	23.52	26.10	31.01
1.08	-	-	19.73	-	-	-
1.13	-	-	20.34	-	-	-
1.19	8.44	17.48	20.95	24.85	27.93	32.03
1.24	-	-	21.26	-	-	-
1.29	-	-	21.77	-	-	-
1.30	-	18.60	-	26.18	29.15	32.85

Contd...

1.34	-	-	21.97	-	-	-
1.39	-	-	22.38	-	-	-
1.41	10.16	19.83	-	26.99	29.87	33.97
1.44	-	-	22.89	-	-	-
1.48	-	-	23.81	-	-	-
1.52	10.87	21.05	-	28.01	30.79	34.38
1.53	-	-	24.22	-	-	-
1.58	-	-	24.83	-	-	-
1.63	11.48	21.77	25.34	29.13	31.70	35.30
1.68	-	-	25.85	-	-	-
1.74	12.30	22.79	-	29.75	32.52	36.32
1.77	-	-	26.26	-	-	-
1.85	12.81	24.01	-	30.56	33.34	36.62
1.86	-	-	26.87	-	-	-
1.95	14.13	25.13	27.38	31.68	34.26	37.85
2.04	-	-	27.99	-	-	-
2.06	14.95	26.25	-	32.50	35.17	38.46
2.12	-	-	28.29	-	-	-
2.16	15.56	26.87	-	33.11	35.99	39.28
2.21	-	-	28.90	-	-	-
2.27	16.18	27.58	-	33.83	36.70	39.68
2.29	-	-	29.62	-	-	-
2.37	16.89	28.50	29.93	34.54	37.42	40.50
2.46	-	-	30.54	-	-	-
2.47	17.80	29.11	-	35.46	37.93	41.11
2.54	-	-	31.05	-	-	-
2.57	18.62	30.13	-	36.07	-	41.72
2.67	-	30.84	-	36.78	-	42.23
2.77	-	31.86	-	37.60	-	-
2.87	20.46	32.88	-	37.80	-	-
2.97	21.48	33.39	-	38.42	-	-
3.07	21.99	34.21	-	39.13	-	-
3.16	22.60	35.13	-	39.54	-	-
3.26	23.01	35.74	-	40.25	-	-
3.35	23.42	36.45	-	40.76	-	-
3.44	24.13	-	-	-	-	-
3.54	24.74	-	-	-	-	-
3.63	25.25	-	-	-	-	-
3.72	25.76	-	-	-	-	-
3.81	26.58	-	-	-	-	-

Contd...

3.92	27.29	-	-	-	-	-
3.99	27.70	-	-	-	-	-
4.07	27.91	-	-	-	-	-
4.16	28.31	-	-	-	-	-
4.25	29.23	-	-	-	-	-
4.34	29.74	-	-	-	-	-
4.67	30.96	-	-	-	-	-
5.00	31.17	-	-	-	-	-

TABLE-3.5.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of tetraethylammonium bromide in water at 25 °C.

C / mM	$\kappa \times 10^4$ / S cm^{-1}					
	x → 0.0	0.4	1.0	2.0	4.0	6.0
0.12	-	5.63	-	-	-	-
0.12	-	-	8.92	13.22	17.32	21.42
0.24	-	6.48	-	-	-	-
0.25	1.85	-	10.04	14.96	18.65	22.15
0.35	-	7.33	-	-	-	-
0.37	-	-	10.85	15.87	20.08	24.18
0.45	-	8.11	-	-	-	-
0.49	3.55	-	12.38	17.10	21.20	25.50
0.55	-	8.85	-	-	-	-
0.61	-	-	13.40	18.42	22.32	26.53
0.65	-	9.49	-	-	-	-
0.73	5.24	-	14.32	19.44	23.55	27.44
0.74	-	10.41	-	-	-	-
0.83	-	11.13	-	-	-	-
0.84	-	-	15.54	20.44	24.46	28.16
0.92	-	11.53	-	-	-	-
0.96	6.86	-	16.46	22.30	25.48	29.28
1.00	-	11.94	-	-	-	-
1.07	-	-	17.38	23.32	26.61	30.09
1.08	-	12.55	-	-	-	-
1.17	-	13.68	-	-	-	-
1.19	8.44	-	18.50	24.03	27.42	31.32
1.23	-	14.29	-	-	-	-
1.29	-	14.90	-	-	-	-
1.30	-	-	19.22	25.05	28.44	31.83
1.36	-	15.41	-	-	-	-
1.41	10.16	-	20.03	25.97	29.05	32.64
1.43	-	15.92	-	-	-	-
1.49	-	16.43	-	-	-	-
1.52	10.87	-	20.64	26.79	30.17	33.66
1.55	-	16.63	-	-	-	-
1.61	-	17.04	-	-	-	-

Contd...

1.63	11.48	-	21.26	27.81	30.99	34.58
1.67	-	17.75	-	-	-	-
1.72	-	18.16	-	-	-	-
1.74	12.30	-	22.07	28.73	31.81	35.4
1.77	-	18.47	-	-	-	-
1.83	-	18.88	-	-	-	-
1.85	12.81	-	22.79	29.95	32.83	36.11
1.88	-	19.39	-	-	-	-
1.92	-	19.49	-	-	-	-
1.95	14.14	-	23.60	30.46	33.44	37.03
1.97	-	19.90	-	-	-	-
2.01	-	20.41	-	-	-	-
2.05	-	20.82	-	-	-	-
2.06	14.95	-	24.11	31.58	34.15	37.85
2.10	-	21.12	-	-	-	-
2.14	-	21.43	-	-	-	-
2.16	15.56	-	24.32	32.50	34.87	38.66
2.18	-	21.53	-	-	-	-
2.22	-	21.84	-	-	-	-
2.26	-	22.14	-	-	-	-
2.27	16.18	-	25.03	33.21	35.68	40.09
2.33	-	22.65	-	-	-	-
2.37	-	22.96	-	-	-	-
2.37	16.89	-	26.05	34.13	36.29	40.91
2.40	-	23.16	-	-	-	-
2.43	-	23.26	-	-	-	-
2.47	17.80	23.47	26.87	34.95	37.42	41.52
2.50	-	23.77	-	-	-	-
2.53	-	23.87	-	-	-	-
2.56	-	24.08	-	-	-	-
2.57	18.62	-	27.48	35.76	38.22	42.13
2.59	-	24.18	-	-	-	-
2.62	-	24.49	-	-	-	-
2.64	-	24.69	-	-	-	-
2.67	-	-	27.99	36.37	-	42.74
2.77	-	-	28.50	37.09	-	-
2.87	20.46	-	28.70	37.90	-	-
2.97	21.48	-	29.21	38.72	-	-
3.07	21.99	-	29.64	39.44	-	-
3.16	22.60	-	30.13	40.05	-	-

Contd...

3.26	23.01	-	30.49	40.66	-	-
3.35	23.42	-	30.95	41.27	-	-
3.44	24.13	-	31.36	41.98	-	-
3.54	24.74	-	31.86	42.06	-	-
3.63	25.25	-	32.38	-	-	-
3.72	25.76	-	-	-	-	-
3.81	26.58	-	-	-	-	-
3.92	27.29	-	-	-	-	-
3.99	27.70	-	-	-	-	-
4.07	27.90	-	-	-	-	-
4.16	28.31	-	-	-	-	-
4.25	29.23	-	-	-	-	-
4.34	29.74	-	-	-	-	-
4.67	30.96	-	-	-	-	-
5.00	31.17	-	-	-	-	-

TABLE-3.6.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of tetra-*n*-propylammonium bromide in water at 25 °C.

C / mM	$\kappa \times 10^4$/S cm^{-1}				
	x → 0.0	1.0	2.0	4.0	6.0
0.12	-	-	8.92	13.12	17.32
0.25	1.85	6.14	10.14	14.75	18.24
0.36	-	-	11.06	-	-
0.37	-	-	-	16.08	19.16
0.48	-	-	11.97	-	-
0.49	3.55	8.48	-	17.30	20.18
0.59	-	-	12.89	-	-
0.61	-	-	-	18.32	21.30
0.71	-	-	13.81	-	-
0.73	5.24	10.52	-	19.55	22.42
0.82	-	-	14.53	-	-
0.84	-	-	-	20.57	23.34
0.92	-	-	15.65	-	-
0.96	6.86	12.06	-	21.58	24.46
1.03	-	-	16.26	-	-
1.07	-	-	-	22.40	25.18
1.14	-	-	17.08	-	-
1.19	8.44	14.20	-	23.52	26.09
1.24	-	-	17.97	-	-
1.30	-	-	-	24.34	26.71
1.34	-	-	18.70	-	-
1.41	10.16	15.93	-	25.26	27.62
1.44	-	-	19.40	-	-
1.52	10.87	16.64	-	25.97	28.44
1.53	-	-	19.93	-	-
1.63	11.48	17.15	20.54	26.99	29.46
1.72	-	-	21.15	-	-
1.74	12.30	18.07	-	27.40	30.28
1.82	-	-	21.56	-	-
1.85	12.81	18.48	-	28.52	31.19
1.91	-	-	22.17	-	-
1.95	14.13	19.19	-	29.34	32.11

Contd...

1.99	-	-	22.99	-	-
2.06	14.95	19.81	-	30.05	32.83
2.08	-	-	23.70	-	-
2.16	15.56	20.32	-	30.76	33.54
2.17	-	-	24.21	-	-
2.25	-	-	24.83	-	-
2.27	16.18	21.03	-	31.68	34.56
2.34	-	-	25.24	-	-
2.37	16.89	21.74	-	32.40	35.17
2.42	-	-	25.64	-	-
2.47	17.80	22.36	-	33.01	35.99
2.50	-	-	26.15	-	-
2.57	18.62	22.76	-	33.72	36.80
2.58	-	-	26.87	-	-
2.66	-	-	27.38	-	-
2.67	-	23.48	-	34.23	37.42
2.73	-	-	28.09	-	-
2.77	-	24.40	-	-	-
2.81	-	-	28.64	-	-
2.87	20.46	24.91	-	-	-
2.88	-	-	29.01	-	-
2.96	-	-	29.83	-	-
2.97	21.48	-	-	-	-
3.03	-	-	30.44	-	-
3.07	21.99	26.23	-	-	-
3.10	-	-	30.64	-	-
3.16	22.60	-	-	-	-
3.26	23.01	27.05	-	-	-
3.35	23.42	-	-	-	-
3.44	24.13	28.07	-	-	-
3.54	24.74	-	-	-	-
3.63	25.25	29.09	-	-	-
3.72	25.76	-	-	-	-
3.81	26.58	-	-	-	-
3.92	27.29	-	-	-	-
3.99	27.70	30.82	-	-	-
4.07	27.90	-	-	-	-
4.16	28.31	31.54	-	-	-
4.25	29.23	-	-	-	-
4.33	-	32.35	-	-	-

Contd...

4.34	29.74	33.37	-	-	-
4.50	-	34.60	-	-	-
4.67	30.96	35.62	-	-	-
4.84	-	-	-	-	-
5.00	31.17	-	-	-	-

TABLE-3.7.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of tetra-*n*-butylammonium bromide in water at 25 °C.

C / mM	$\kappa \times 10^4$/S cm^{-1}					
	x → 0.0	0.5	1.0	2.0	4.0	6.0
0.06	-	-	-	-	-	25.61
0.02	-	-	-	-	20.08	-
0.12	-	-	-	13.12	-	26.02
0.18	-	-	-	-	-	26.63
0.24	-	-	-	-	22.45	-
0.25	1.85	6.20	10.14	14.65	-	26.73
0.31	-	-	-	-	-	27.34
0.33	-	-	-	-	22.35	-
0.37	-	-	-	15.77	-	27.65
0.41	-	-	-	-	23.97	-
0.43	-	-	-	-	-	27.95
0.48	-	-	-	-	23.60	-
0.49	3.55	8.28	12.28	16.69	-	28.36
0.55	-	-	-	-	-	28.67
0.56	-	-	-	-	25.20	-
0.61	-	-	-	17.61	-	29.08
0.64	-	-	-	-	24.70	-
0.67	-	-	-	-	-	29.38
0.72	-	-	-	-	25.40	-
0.73	5.24	10.12	13.91	18.73	-	29.59
0.78	-	-	-	-	-	29.79
0.84	-	-	-	19.85	-	30.50
0.87	-	-	-	-	26.40	-
0.90	-	-	-	-	-	30.71
0.94	-	-	-	-	26.90	-
0.96	6.86	11.85	15.44	20.87	-	31.01
1.01	-	-	-	-	-	31.32
1.07	-	-	-	20.89	-	31.63
1.09	-	-	-	-	28.20	-
1.13	-	-	-	-	-	32.14
1.16	-	-	-	-	28.60	-
1.19	8.44	13.69	17.48	22.81	-	-

Contd...

1.23	-	-	-	-	29.10	-
1.30	-	-	-	23.83	29.40	33.06
1.35	-	-	-	-	-	33.46
1.41	10.16	15.63	19.01	24.44	-	33.77
1.44	-	-	-	-	30.50	-
1.47	-	-	-	-	-	33.77
1.51	-	-	-	-	31.20	-
1.52	10.87	-	-	25.36	-	34.59
1.58	-	-	-	-	31.70	34.79
1.63	11.48	16.95	20.54	26.28	-	35.09
1.65	-	-	-	-	32.00	-
1.68	-	-	-	-	-	36.81
1.72	-	-	-	-	32.70	-
1.74	12.30	-	-	27.19	-	36.01
1.78	-	-	-	-	33.00	-
1.79	-	-	-	-	-	36.52
1.85	12.81	18.89	22.17	28.11	33.40	36.63
1.90	-	-	-	-	-	36.84
1.91	-	-	-	-	33.90	-
1.95	14.13	-	-	29.13	-	37.59
1.98	-	-	-	-	34.30	-
2.04	-	-	-	-	34.70	-
2.06	14.95	20.32	23.50	30.36	-	37.75
2.11	-	-	-	-	35.20	-
2.16	15.56	-	-	30.87	-	38.26
2.23	-	-	-	-	36.10	-
2.27	16.17	21.85	25.03	31.99	-	38.66
2.37	16.89	-	-	32.80	-	39.18
2.47	17.80	23.17	26.36	33.72	-	40.09
2.57	18.62	-	-	34.54	-	40.50
2.67	-	24.19	28.09	35.35	-	40.91
2.77	-	-	-	36.17	-	41.52
2.87	20.46	25.62	29.21	37.19	-	42.24
2.97	21.48	-	-	37.70	-	42.74
3.07	21.99	26.64	30.50	38.72	-	-
3.16	22.60	-	-	-	-	-
3.26	23.01	29.29	31.56	-	-	-
3.35	23.42	-	-	-	-	-
3.44	24.13	30.11	32.99	-	-	-
3.54	24.74	-	-	-	-	-

Contd...

3.63	25.25	31.54	34.21	-	-	-
3.72	25.76	-	-	-	-	-
3.81	26.58	-	-	-	-	-
3.84	-	32.56	35.23	-	-	-
3.92	27.29	-	-	-	-	-
3.99	27.70	33.88	36.96	-	-	-
4.07	27.90	-	-	-	-	-
4.16	28.31	35.00	38.09	-	-	-
4.33	-	36.13	39.31	-	-	-
4.34	29.74	-	-	-	-	-
4.50	-	36.74	40.50	-	-	-
4.674	30.96	37.96	-	-	-	-
5.00	31.17	-	-	-	-	-

TABLE-3.8.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of tetra-*n*-butylphosphonium bromide in water at 25 °C.

C / Mm	$\kappa \times 10^4$/S cm^{-1}			
	x → 0.0	0.5	1.0	2.0
0.06	-	4.56	-	16.51
0.12	-	-	9.42	16.92
0.13	-	4.99	-	-
0.18	-	-	-	17.42
0.19	-	5.70	-	-
0.25	1.85	-	11.57	17.83
0.25	-	6.19	-	-
0.31	-	-	-	18.24
0.31	-	6.75	-	-
0.37	-	-	12.08	18.65
0.38	-	7.26	-	-
0.43	-	-	-	19.06
0.44	-	7.74	-	-
0.49	3.56	-	13.30	19.44
0.50	-	8.08	-	-
0.55	-	-	-	19.77
0.56	-	8.38	-	-
0.61	-	-	14.42	20.18
0.62	-	8.99	-	-
0.67	-	-	-	20.59
0.68	-	9.61	-	-
0.73	5.24	-	15.34	20.79
0.74	-	9.91	-	-
0.78	-	-	-	21.10
0.80	-	10.42	-	-
0.84	-	-	16.67	21.61
0.86	-	11.00	-	-
0.90	-	-	-	21.91
0.92	-	11.44	-	-
0.96	6.86	-	17.58	22.32
0.98	-	11.95	-	-
1.02	-	-	-	22.83

Contd..

1.04	-	12.46	-	-
1.07	-	-	18.50	23.03
1.10	-	12.97	-	-
1.13	-	-	-	23.44
1.19	8.44	-	19.73	-
1.21	-	13.69	-	-
1.28	-	14.09	-	-
1.30	-	-	20.64	-
1.33	-	14.60	-	-
1.39	-	15.00	-	-
1.41	10.16	-	21.87	-
1.44	-	15.49	-	-
1.50	-	15.73	-	-
1.52	10.87	-	22.58	-
1.56	-	16.44	-	-
1.61	-	16.95	-	-
1.63	11.48	-	23.70	-
1.67	-	17.54	-	-
1.73	-	17.97	-	-
1.74	12.30	-	24.62	-
1.78	-	18.17	-	-
1.84	-	18.58	-	-
1.85	12.81	-	25.30	-
1.89	-	18.99	-	-
1.95	14.13	19.70	26.76	-
2.00	-	20.00	-	-
2.06	-	20.32	-	-
2.06	14.95	-	-	-
2.11	-	20.83	-	-
2.16	15.56	21.23	-	-
2.21	-	21.34	-	-
2.27	-	21.74	-	-
2.32	-	22.25	-	-
2.37	16.89	-	-	-
2.38	-	22.66	-	-
2.43	-	23.07	-	-
2.47	17.80	-	-	-
2.53	-	23.68	-	-
2.57	18.62	-	-	-
2.64	-	24.70	-	-

Contd...

2.67	-	25.31	-	-
2.86	-	26.13	-	-
2.87	20.46	-	-	-
2.94	-	26.64	-	-
2.97	21.48	-	-	-
3.07	21.99	-	-	-
3.16	22.60	-	-	-
3.26	23.01	-	-	-
3.35	23.42	-	-	-
3.44	24.13	-	-	-
3.54	24.74	-	-	-
3.63	25.25	-	-	-
3.72	27.76	-	-	-
3.81	26.58	-	-	-
3.92	27.29	-	-	-
3.99	27.70	-	-	-
4.07	27.90	-	-	-
4.16	28.31	-	-	-
4.34	29.74	-	-	-
4.67	30.96	-	-	-
5.00	31.17	-	-	-

TABLE-3.9.

Variation of specific conductivity, κ, with concentration, C, of SDBS in different concentrations (x mM) of tetraphenylphosphonium bromide in water at 25 °C.

C / mM	$\kappa \times 10^4$/S cm^{-1}			
	x → 0.0	0.5	0.7	0.9
0.12	-	-	-	12.84
0.24	1.85	5.74	9.68	13.63
0.37	-	-	-	14.57
0.49	3.55	7.31	11.11	15.28
0.61	-	-	-	15.99
0.73	5.24	8.78	12.67	16.81
0.84	-	-	-	17.42
0.96	6.86	10.47	14.09	18.24
1.07	-	-	-	18.95
1.19	8.44	11.90	15.42	19.56
1.30	-	-	-	20.00
1.41	10.15	13.23	16.85	20.79
1.52	10.87	-	-	21.71
1.63	11.48	14.86	18.18	22.32
1.74	12.30	-	-	23.13
1.85	12.81	16.29	19.60	23.75
1.95	14.13	-	-	24.56
2.06	14.95	17.71	20.72	25.48
2.16	15.56	-	-	25.99
2.27	16.17	18.97	22.00	26.60
2.37	16.89	-	-	27.30
2.47	17.80	20.57	23.48	-
2.57	18.62	-	-	-
2.67	-	21.28	24.60	-
2.87	20.46	22.81	25.62	-
2.97	21.48	-	-	-
3.07	21.99	24.14	-	-
3.26	23.01	25.36	28.27	-
3.35	23.42	-	-	-
3.44	24.13	26.69	29.39	-
3.54	24.74	-	-	-
3.63	25.25	27.71	30.92	-

Contd...

3.72	25.76	-	-	-
3.81	26.58	28.93	32.05	-
3.92	27.29	-	-	-
3.99	27.70	30.06	-	-
4.07	27.90	-	-	-
4.16	28.31	30.87	-	-
4.33	29.74	32.02	-	-
4.67	30.96	-	-	-
5.00	31.17	-	-	-

TABLE-3.10.

cmc values of SDBS with concentration of different salts in water at 25 °C.

[Salt] / mM	cmc / mM		
	LiBr	NaBr	Bu_4NBr
0.5	-	-	1.62
1.0	-	-	1.44
2.0	-	-	1.28
4.0	1.82	1.60	0.71
6.0	1.70	1.12	0.47
8.0	1.52	0.53	-

cmc = 2.50 mM in water without any added salt.

TABLE-3.11.

cmc values of SDBS with concentration of different quaternary bromides in water at 25 °C.

[Salt]/ mM	cmc / mM				
	NH_4Br	Me_4NBr	Et_4NBr	Pr_4NBr	Bu_4NBr
0.4	-	1.01	1.56	-	-
0.5	-	-	-	-	1.62
1.0	-	0.94	1.16	1.33	1.44
2.0	-	0.85	0.84	1.20	1.28
4.0	1.54	0.58	0.66	0.84	0.71
5.0	1.48	-	-	-	-
6.0	1.03	0.58	0.54	0.64	0.47

TABLE-3.12.

cmc values of SDBS with concentration of different quaternary bromides in water at 25 °C.

[Salt] / mM	cmc / mM		
	Bu_4NBr	Bu_4PBr	ϕ_4PBr
0.5	1.62	1.40	2.23
0.7	-	-	1.97
0.9	-	-	1.06
1.0	1.44	0.64	-
2.0	1.28	0.45	-
4.0	0.71	-	-
6.0	0.47	-	-

TABLE - 3.13

Variation of the degree of dissociation (α) of SDBS micelles as a function of concentration and nature of the salts.

[Salt] / mM	LiBr	NaBr	NH_4Br	Me_4NBr	Et_4NBr	Pr_4NBr	Bu_4NBr	Bu_4PBr	ϕ_4PBr
0.4				0.81	0.80				
0.5							0.84	0.88	0.77
0.7									0.78
0.9									0.77
1.0				0.80	0.82	0.77	0.81	0.83	
2.0				0.79	0.78	0.78	0.85	0.84	
4.0	0.89	0.78	0.84	0.78	0.69	0.72	0.76		
5.0			0.81						
6.0	0.92	0.77	0.78	0.78	0.62	0.76	0.78		
8.0	0.91	0.75							

α = 0.86 in water without any added salt.

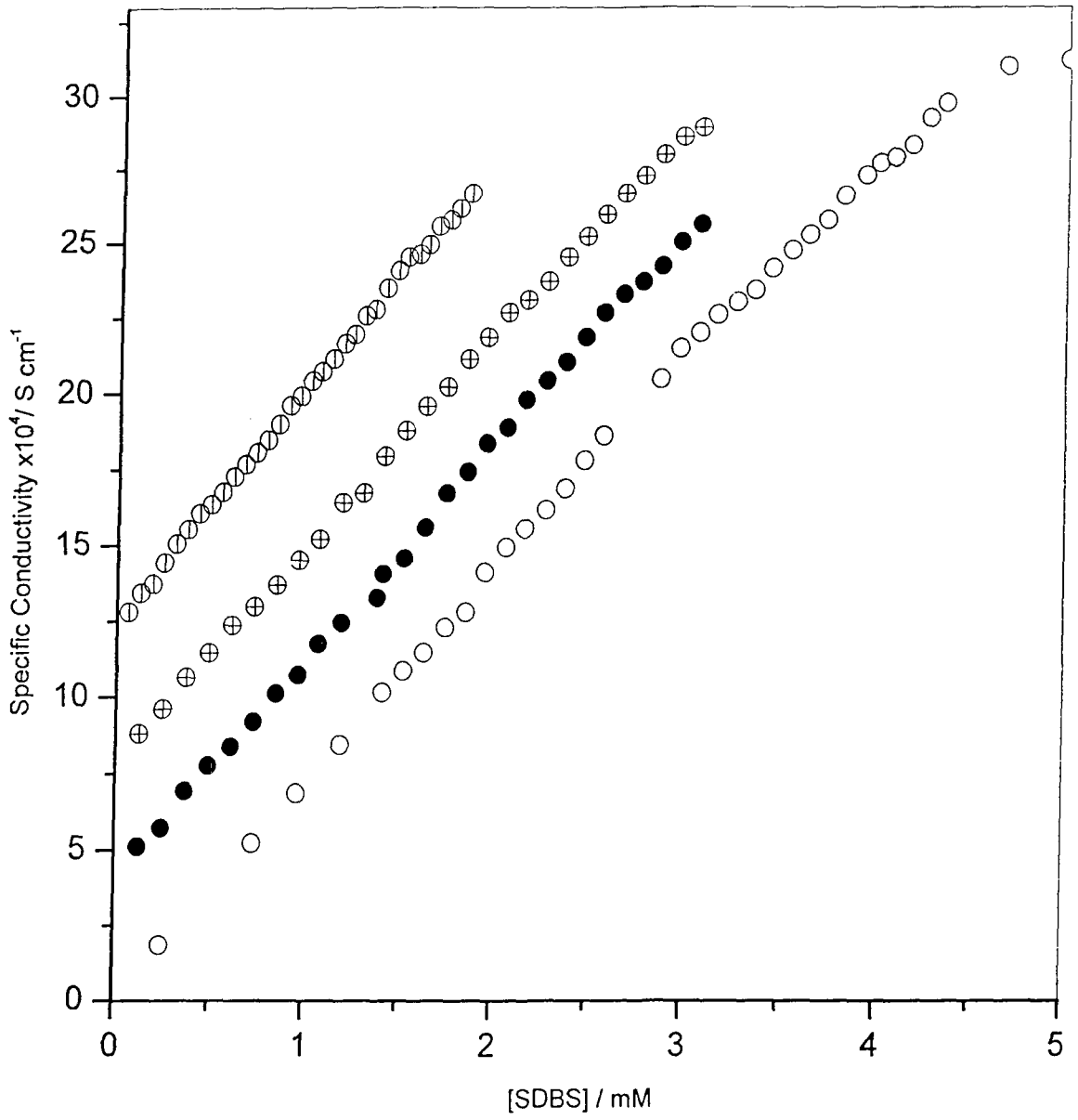

Fig. 3.1. Plots of specific conductivity (κ) *vs.* [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●), 4.0; (⊕), 6.0; (Φ), 8.0 mM LiBr. The plots are shifted vertically by 4, 8 and 12 units, respectively, for clarity of presentation.

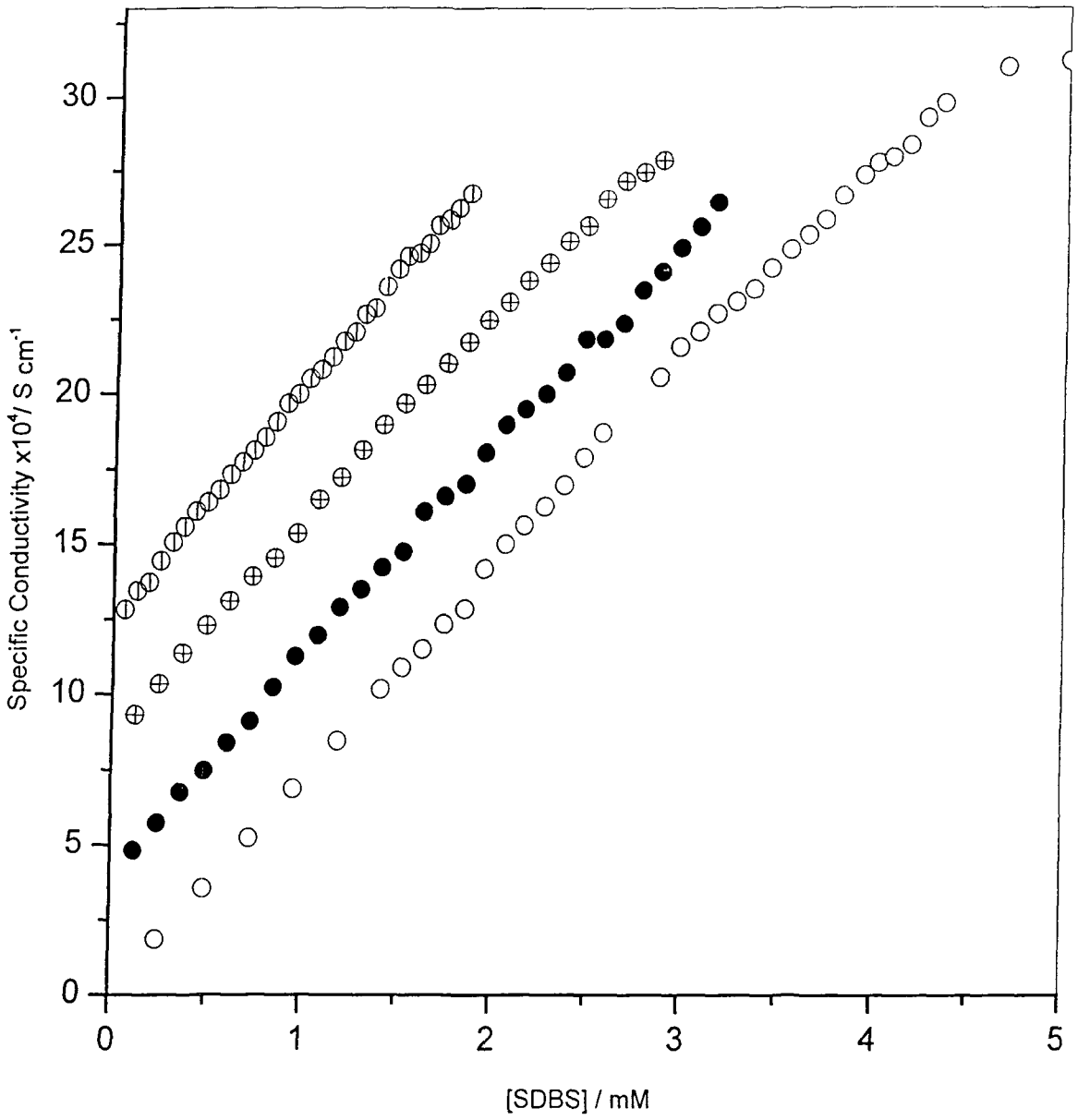

Fig. 3.2. Plots of specific conductivity (κ) *vs.* [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●), 4.0; (⊕), 6.0; (Φ), 8.0 mM NaBr. The plots are shifted vertically by 4, 8 and 12 units, respectively, for clarity of presentation.

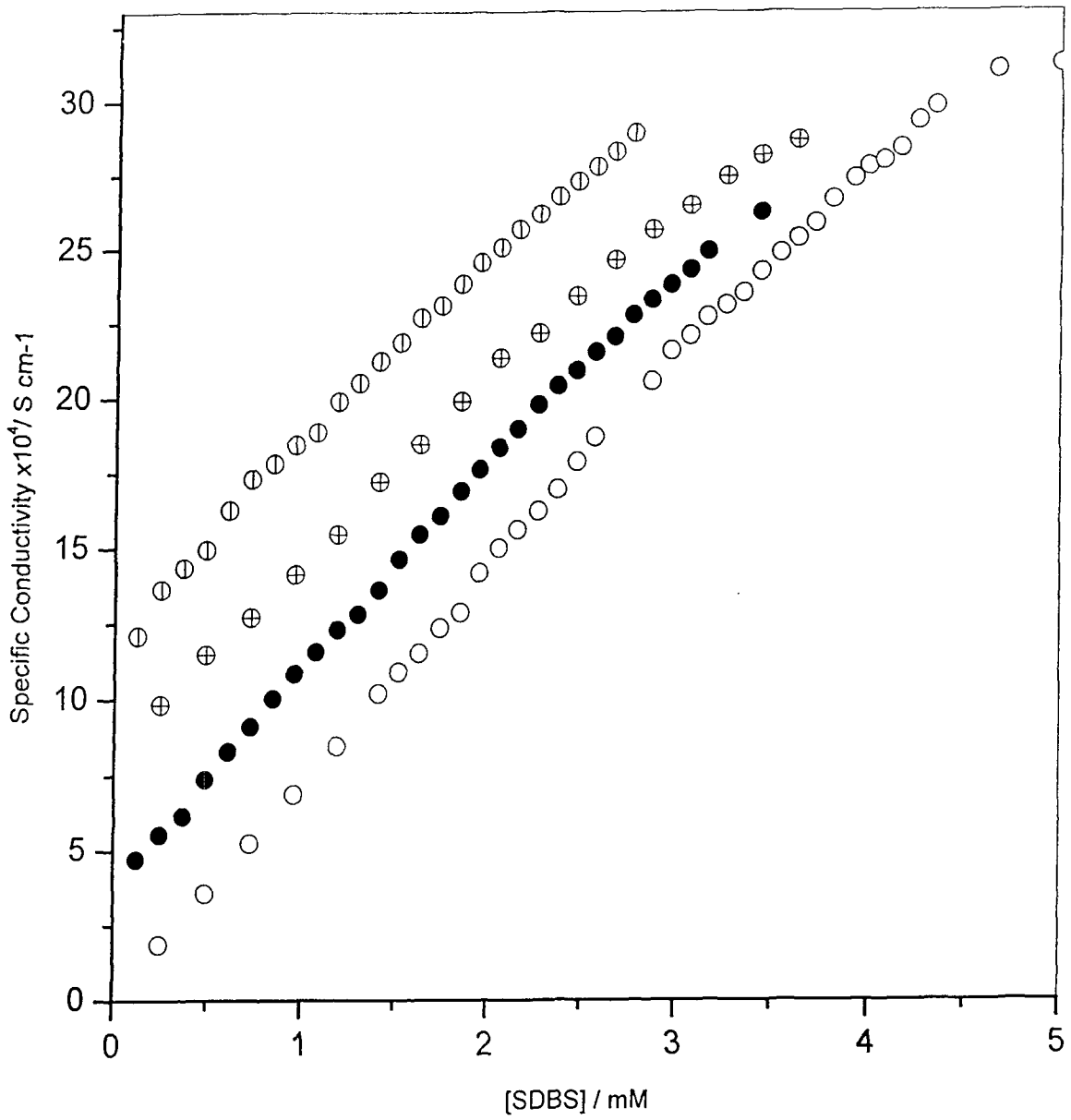

Fig. 3.3. *Plots of specific conductivity (κ) vs. [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●), 4.0; (⊕), 5.0; (⊖), 6.0 mM NH_4Br. The plots are shifted vertically by 4, 8 and 12 units, respectively, for clarity of presentation.*

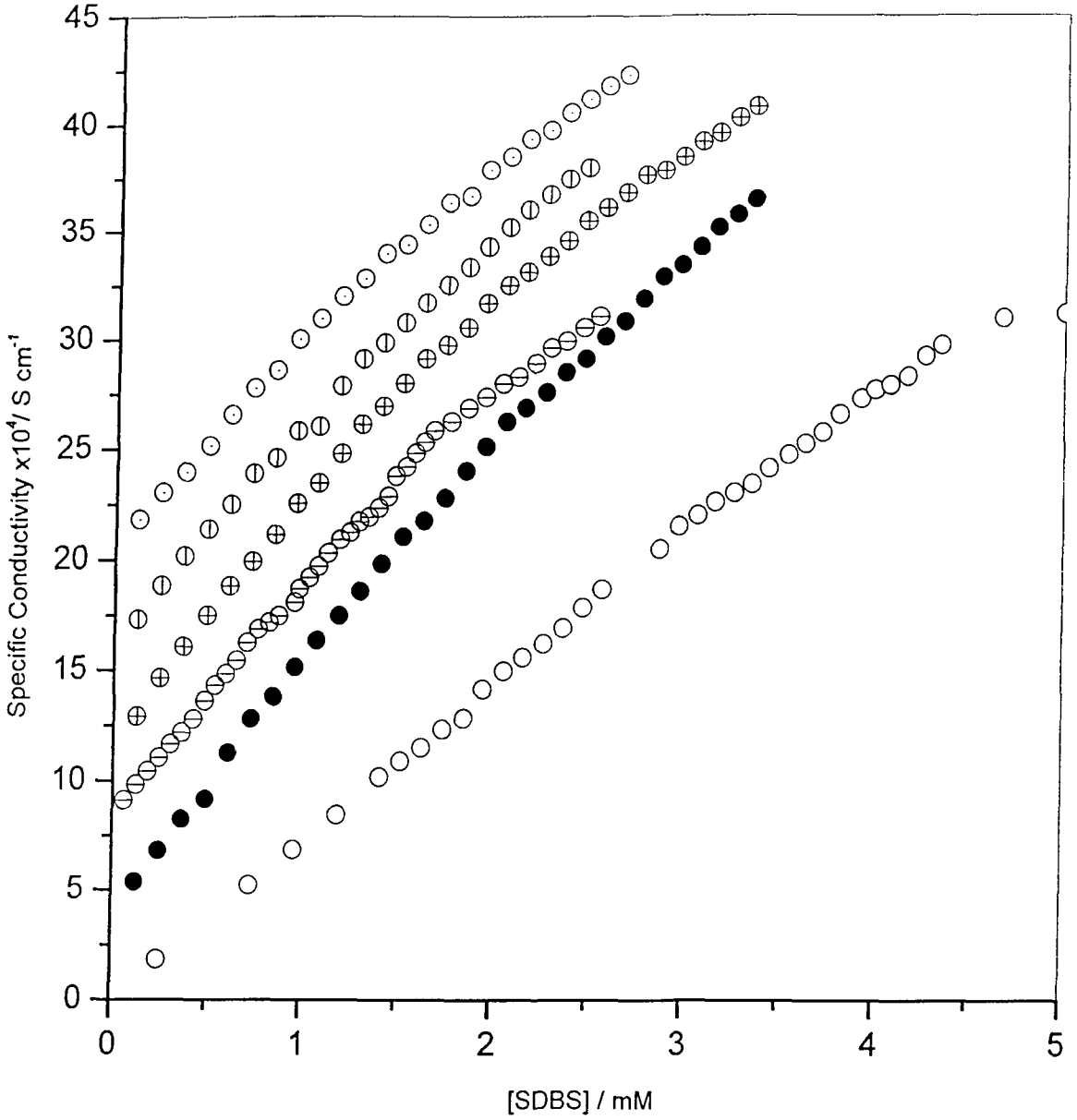

Fig. 3.4. Plots of specific conductivity (κ) *vs.* [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●), 0.4; (⊖), 1.0; (⊕), 2.0; (⊙), 4.0; (⊙), 6.0 mM Me_4NBr. The plots are shifted vertically by 0, 4, 8, 12, 16 and 20 units, respectively, for clarity of presentation.

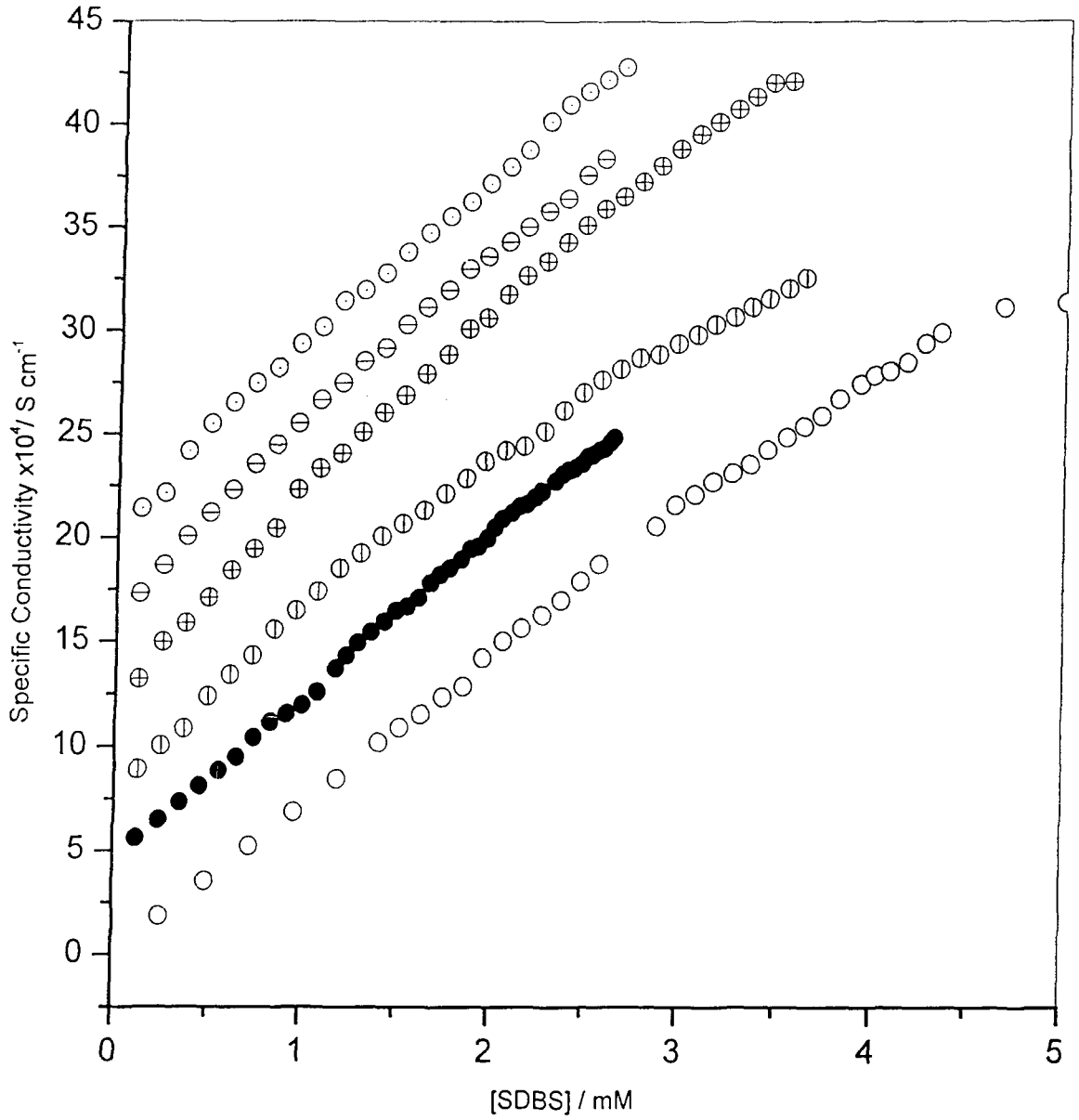

Fig. 3.5. Plots of specific conductivity (κ) *vs.* [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●), 0.4; (⊕), 1.0; (⊕), 2.0; (⊖), 4.0; (⊙), 6.0 mM Et_4NBr. The plots are shifted vertically by 0, 4, 8, 12, 16 and 20 units, respectively, for clarity of presentation.

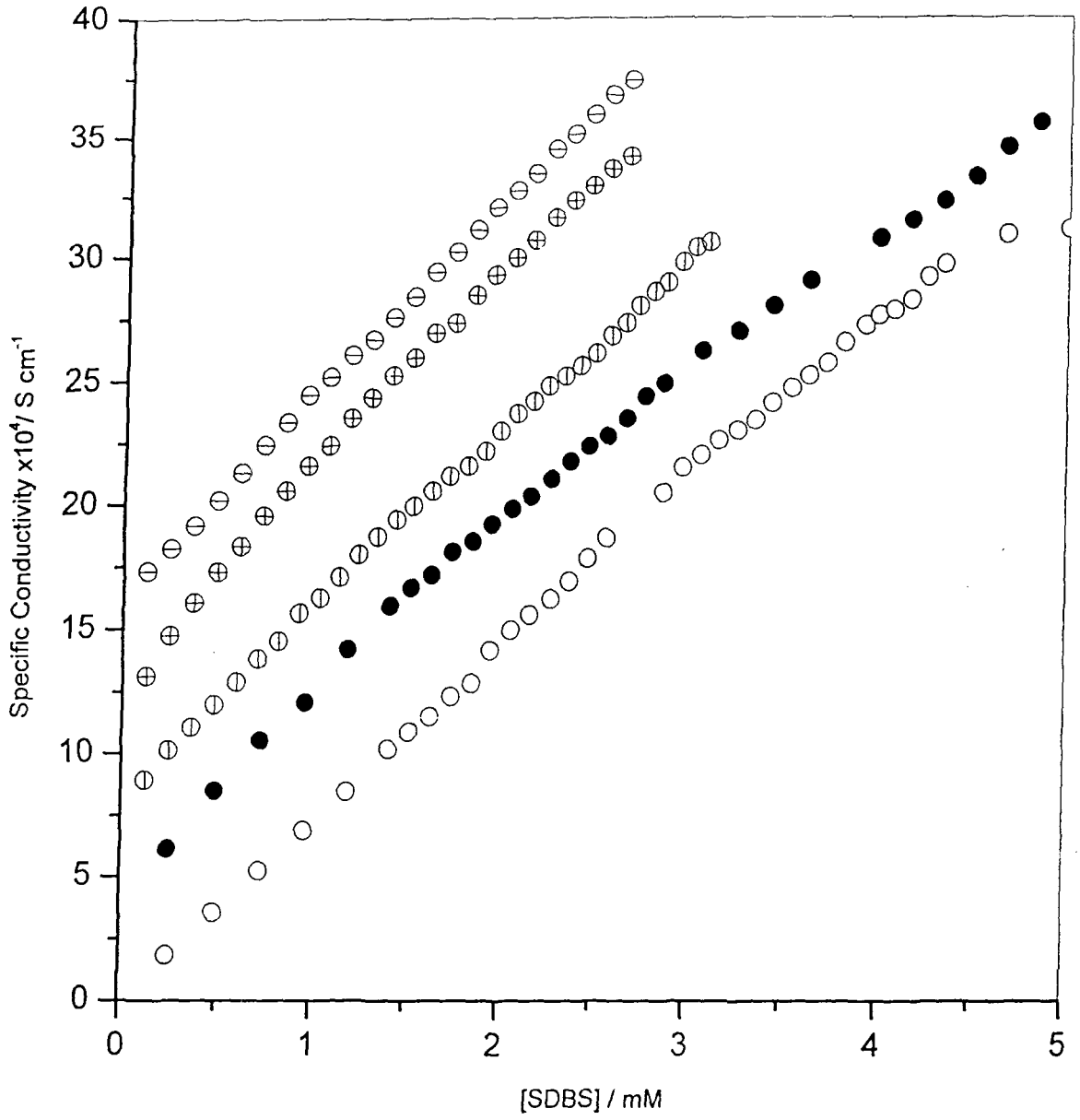

Fig. 3.6. *Plots of specific conductivity (κ) vs. [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●),1.0; (⊖), 2.0; (⊕), 4.0; (⊖), 6.0 mM Pr_4NBr. The plots are shifted vertically by 0, 4, 8, 12 and 16 units, respectively, for clarity of presentation.*

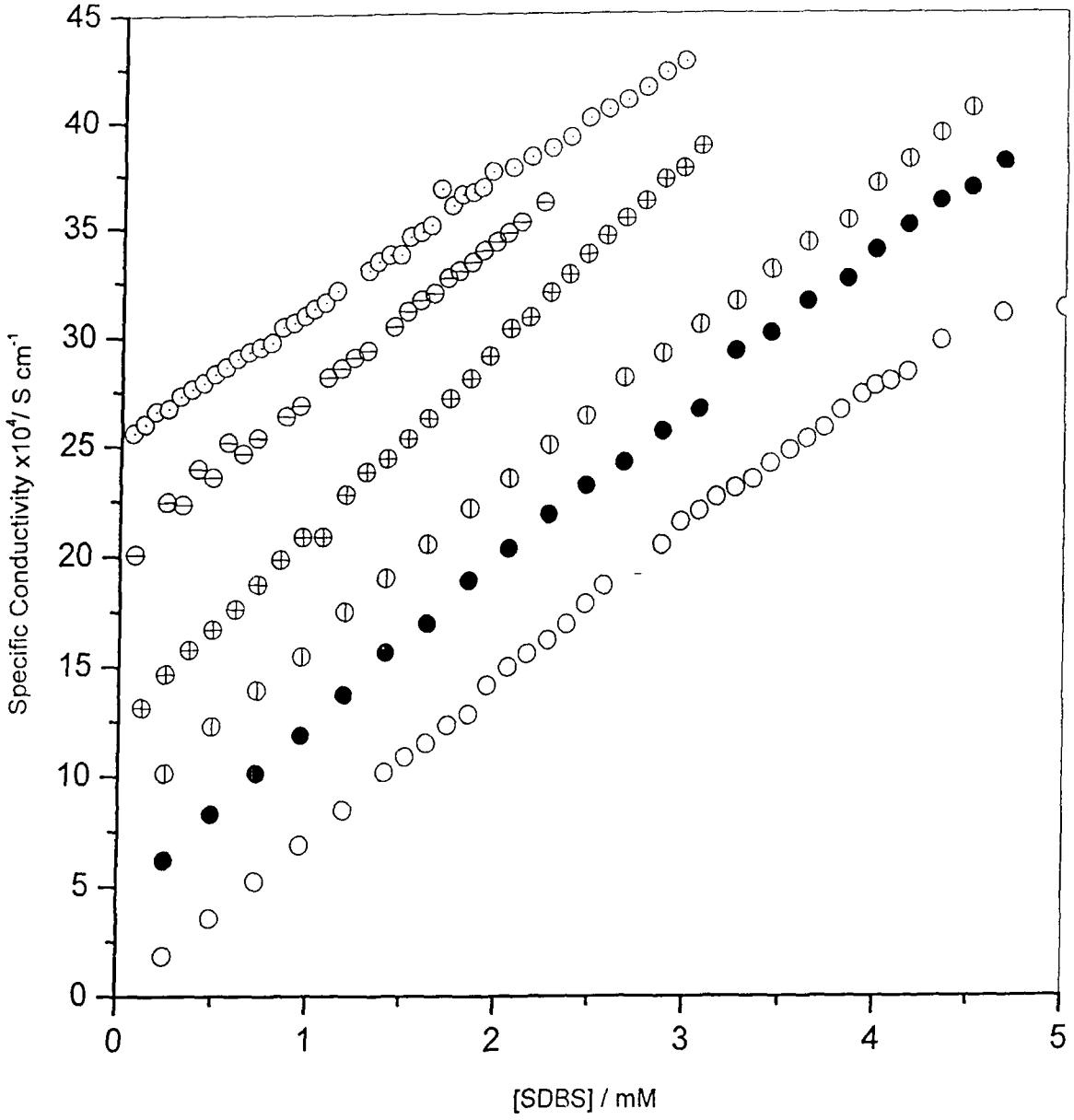

Fig. 3.7. Plots of specific conductivity (κ) *vs.* [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●), 0.5; (⊕), 1.0; (⊕), 2.0; (⊖), 4.0; (⊙), 6.0 mM Bu_4NBr. The plots are shifted vertically by 0, 4, 8, 12, 16 and 20 units, respectively, for clarity of presentation.

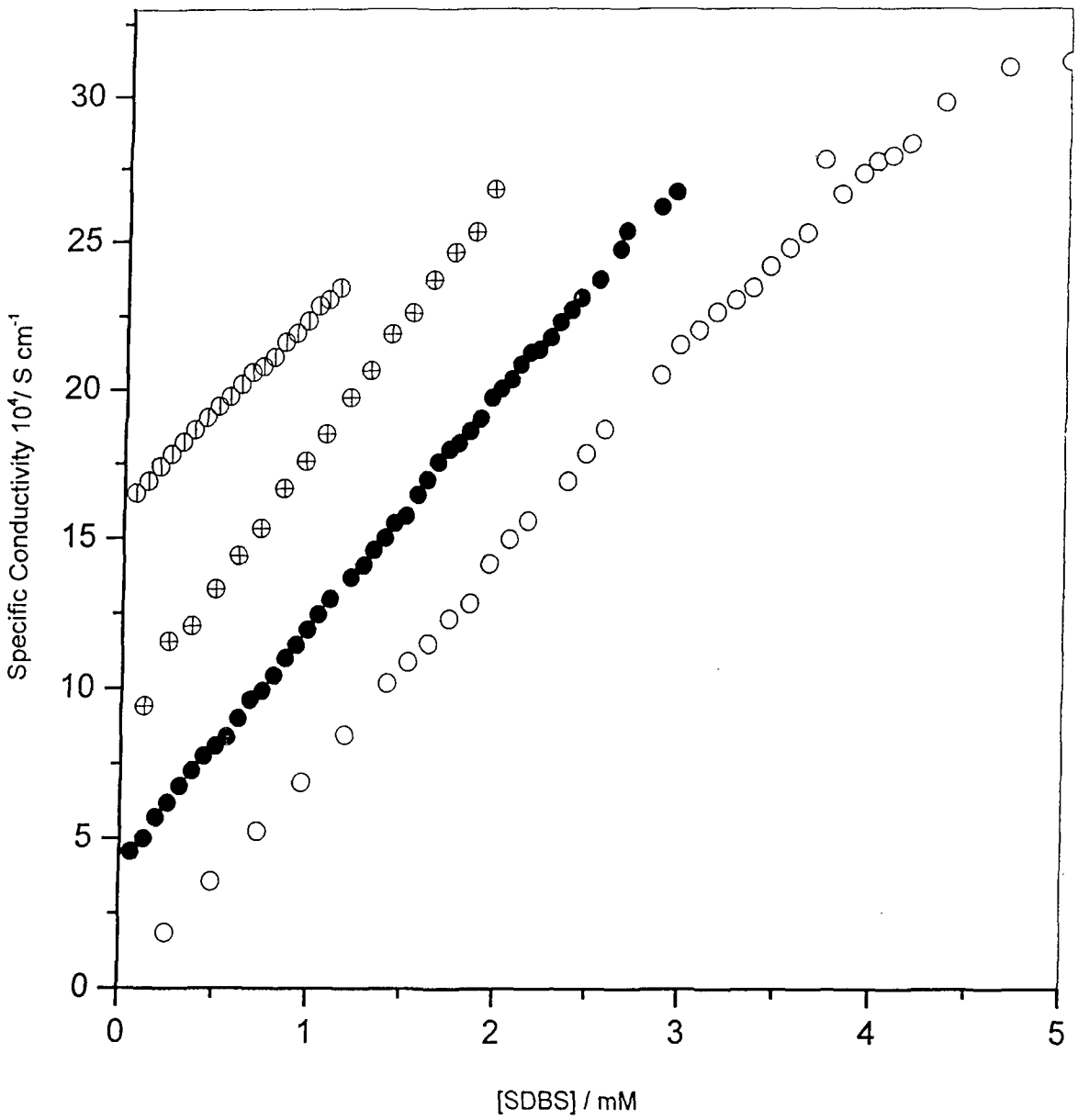

Fig. 3.8. Plots of specific conductivity (κ) *vs.* [SDBS] in aqueous and aqueous salt solutions at 25 °C : (○), no salt; (●), 0.5; (⊕), 1.0; (⊙), 2.0 mM Bu_4PBr. The plots are shifted vertically by 0, 4, 8 and 12 units, respectively, for clarity of presentation.

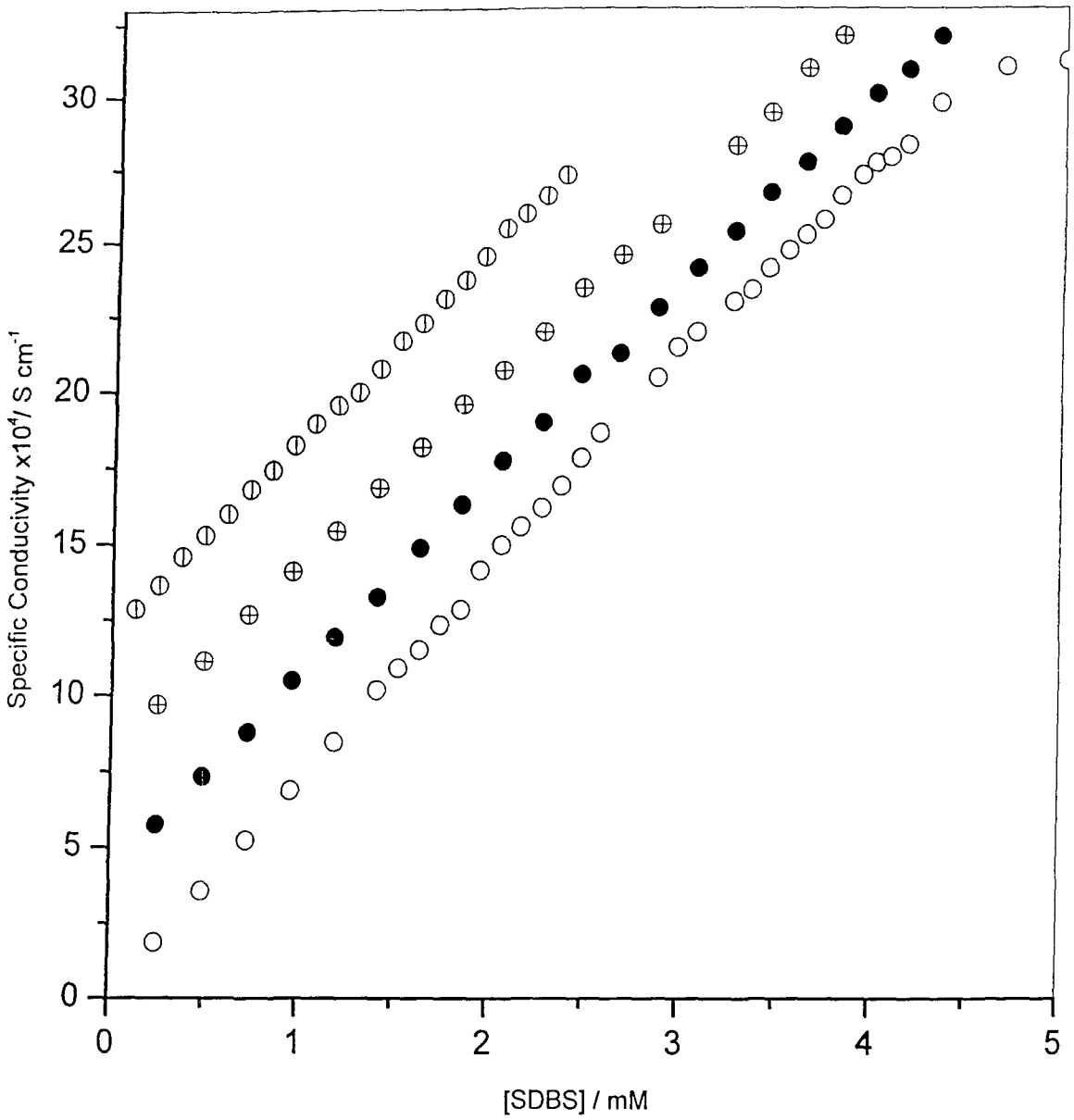

Fig. 3.9. Plots of specific conductivity (κ) *vs.* [SDBS] in aqueous and aqueous salt solutions at 25°C : (○), no salt; (●), 0.5; (⊕), 0.7; (⊙), 0.9 mM ϕ_4PBr. The plots are shifted vertically by 4, 8 and 12 units, respectively, for clarity of presentation.

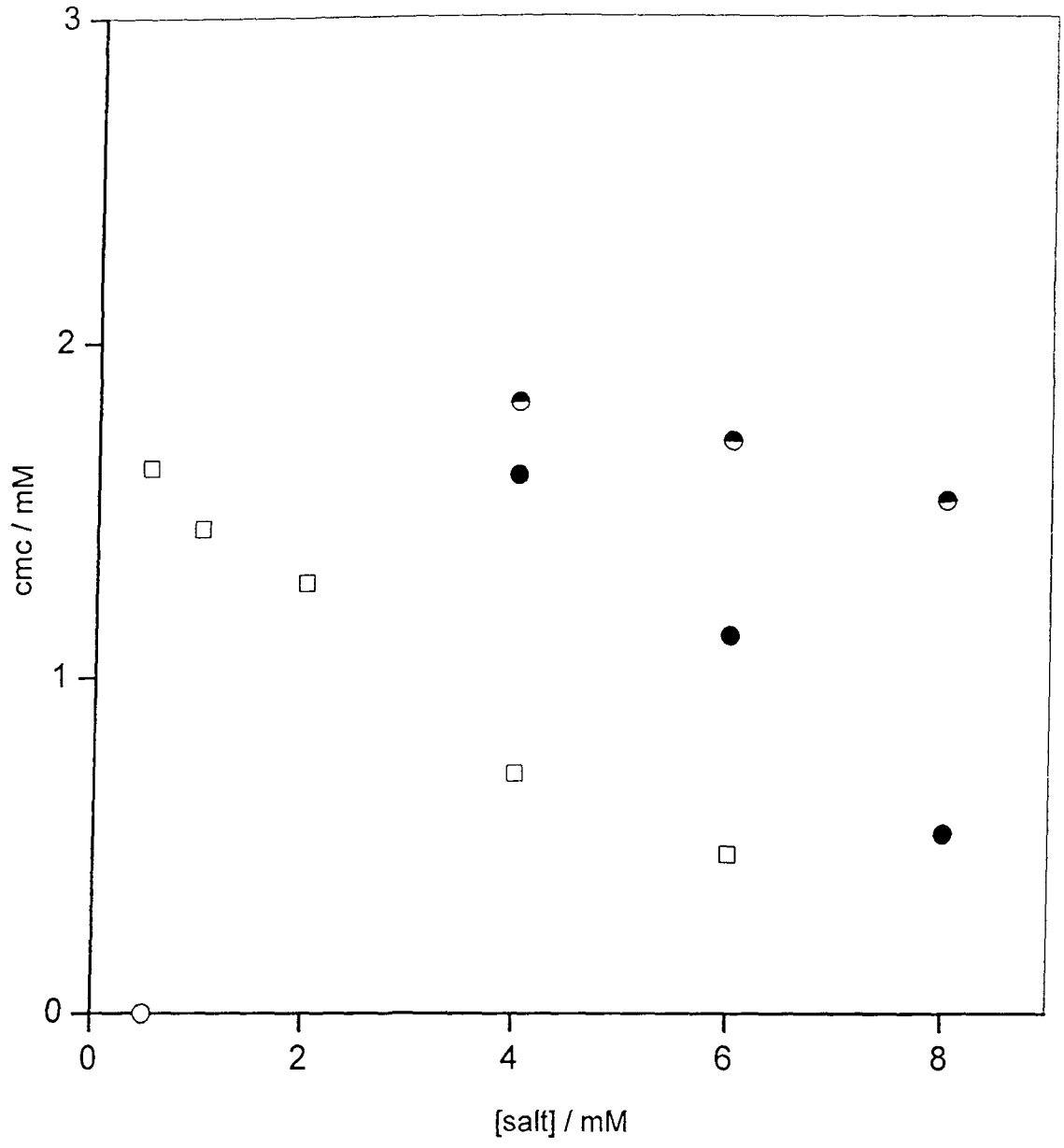

Fig. 3.10. Variation of cmc of SDBS with salt concentration : (◓), LiBr; (●), NaBr; (□), Bu_4NBr

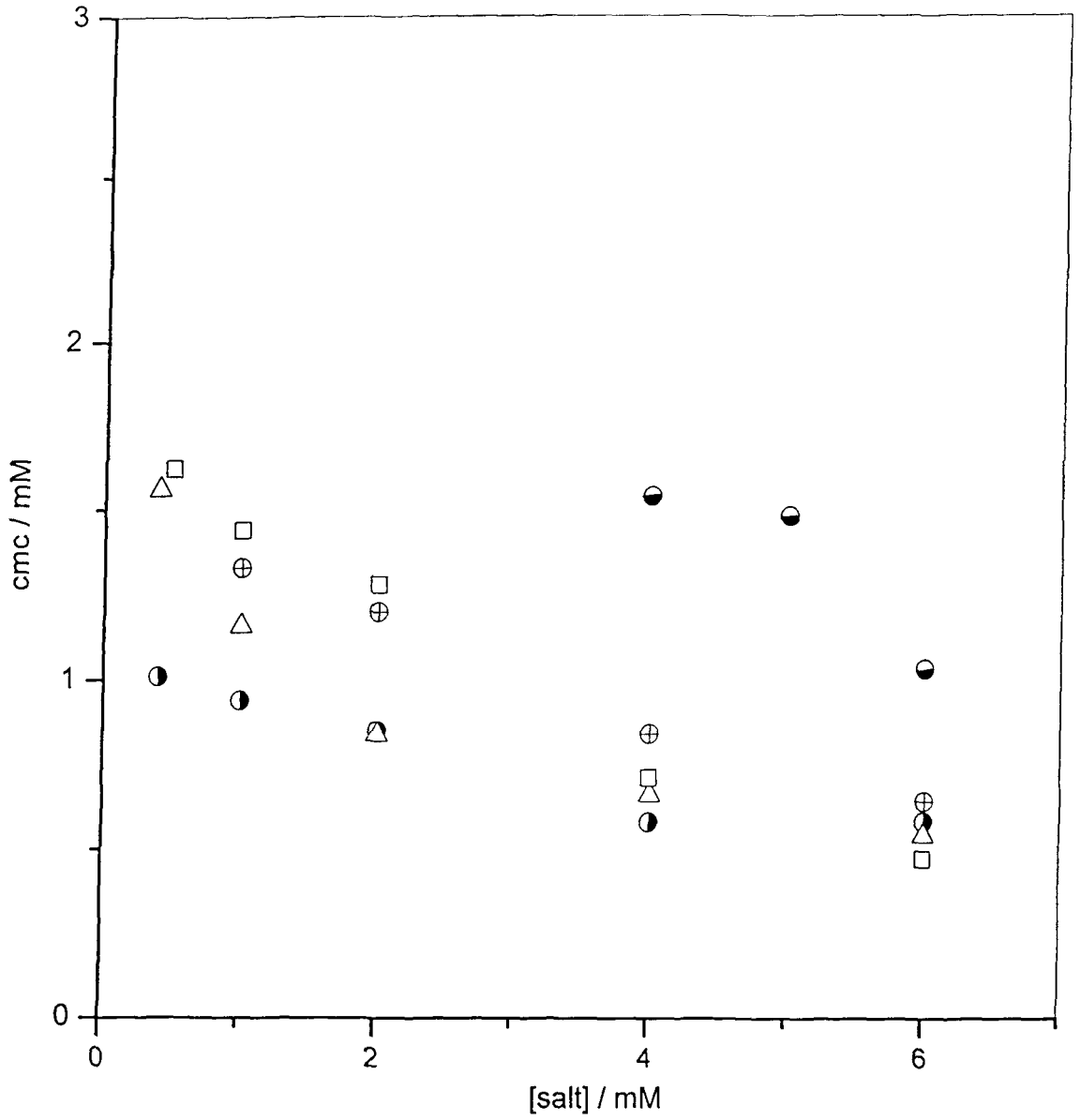

Fig. 3.11. Variation of cmc of SDBS with salt concentration of quaternary bromides : (◒), NH_4Br; (◑), Me_4NBr; (△), Et_4NBr; (⊕), Pr_4NBr; (□), Bu_4NBr.

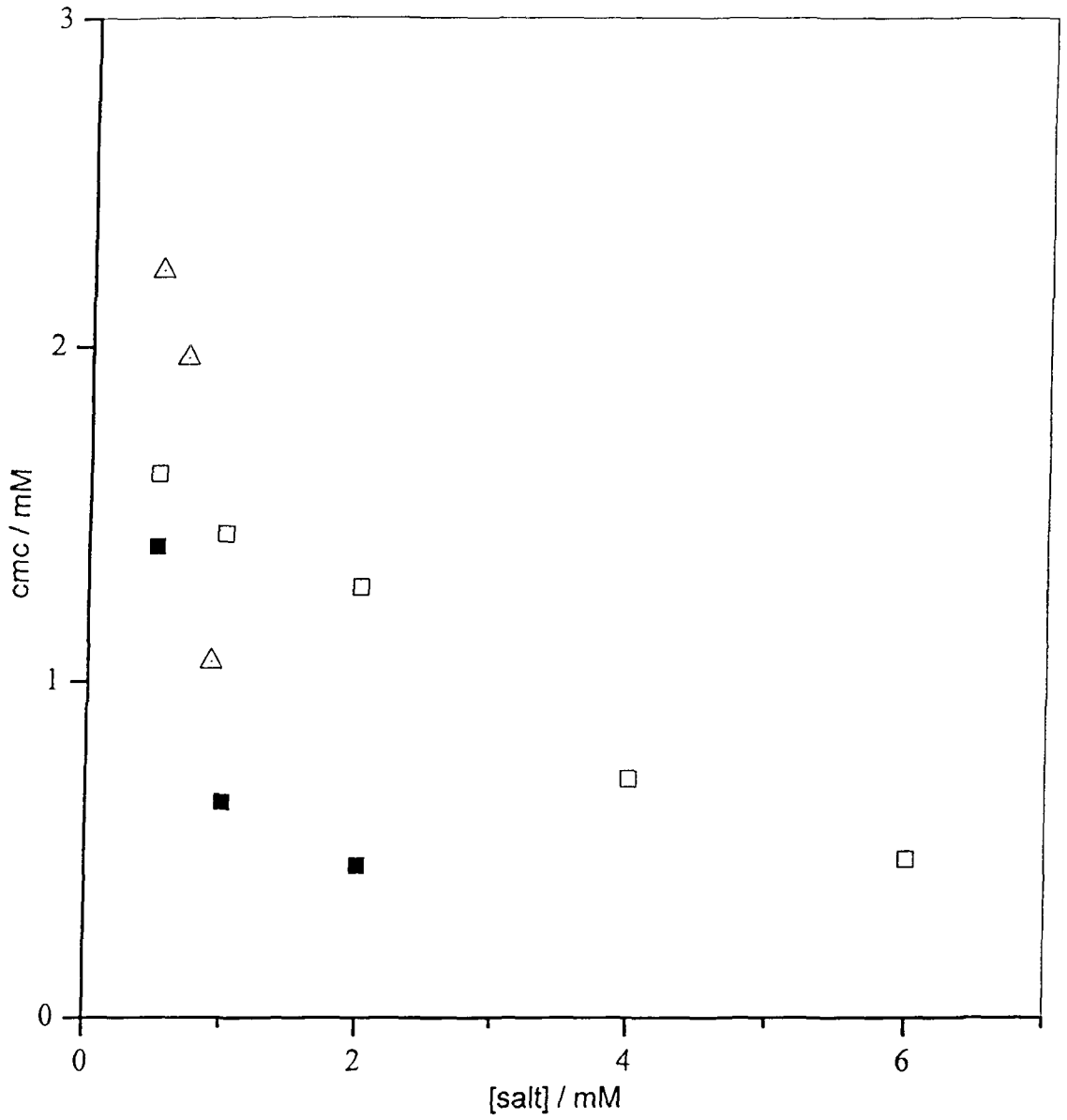

Fig. 3.12. Variation of cmc of SDBS with salt concentration of quaternary bromides having bulky counterions: (□), Bu_4N^+; (■), Bu_4P^+; (△), ϕ_4P^+.

illustrated in Figs. 3.10-3.12. The corresponding cmc and α-values for each SDBS - [salt] combination are summarized in Tables 3.10-3.13.

DISCUSSION

The conductivity can be linearly correlated to the [surfactant] in both the pre-micellar and post-micellar regions,[18] having a slope in the pre-micellar region greater than that in the post-micellar region. Intersection point between the two straight lines gives the cmc and the ratio of the slopes gives the degree of counterion dissociation (α). The specific conductivity *vs.* [SDBS] plots for different inorganic as well as quaternary salts, shown in Figs. 3.1-3.9, were used to find the values (Tables 3.10-3.13).

Before discussing the role of salt counterions on cmc, it is worthwhile to comment about possible influence a counterion may have near the micellar surface. Inorganic counterions (e.g., Li^+ or Na^+) are strongly hydrated,[19] and behave as if they are large. Counterions are 'bound' to micelles primarily by the strong electrical field created by the headgroups, but also by specific interactions that depend upon the headgroup and the counterion type. Specific counterion effects on a variety of micellar properties generally follow a Hofmeister series.[20] Moreover, specificity may also depend upon the partial disruption of the hydration layers of the headgroups and counterions. The locations of headgroups and distributions of counterions within the interfacial region can not be determined precisely because micelles are dynamic aggregates and the boundaries of the interfacial region depend to some extent on the components present in the aggregate. Specific counterions are polarizable with a low charge density,[21,22] and interact strongly with the micellar surface. Because of their nature, the specific counterions are likely to be located in an inner region with respect to simple alkali metal counterions, which are less close to the

surface. Most probably, the specific counterions are in between the headgroups, while the latter ones are in front of them. However, quaternary ammonium counterions are considered as if wrapped in a plastic bag and, therefore, can interact specifically – only electrostatically with anionic headgroups and hydrophobically with exposed hydrocarbon chains. Also, the repulsive force between similar hydrated ions appears to increase on going from K^+- K^+ to Li^+- Li^+.[23] Therefore, repulsion between R_4N^+- Na^+ can be expected to be less than Na^+- Na^+ with concomitant increased binding to the anionic sulfonate headgroup. With this information we shall discuss the effect of various salts on the cmc of SDBS in the paragraphs that follow.

Figure 3.10 shows the variation of cmc of SDBS as a function of added [salt] at 25 °C. We can see that the rate of cmc decrease with [salt] is steeper with Bu_4NBr in comparison to NaBr. Table 3.14 shows the hydrated radii (r_h) and solvation layer thicknesses (**t**) of some alkali metal and R_4N^+ cations. The nonhydrated ion size of inorganic counterions are smaller than that of Bu_4N^+. For the present data one must remember that cmc may also depend upon hydration state of counterions and headgroups, in addition to that of counterion size and their electrostatic interaction with headgroups. Hence cmc may decrease not only due to electrostatic interaction but also due to weakening of the hydration of the hydrophilic groups[24] (or by reducing the number of the hydrating water molecules surrounding the headgroups). The butyl chains in Bu_4N^+ may also interact hydrophobically. All the above effects are seemingly operative in the present case and are responsible for the greater lowering of SDBS cmc with Bu_4NBr. Similar results were obtained earlier in case of the sodium dodecylsulfate.[25]

The cmc variation in presence of R_4NBr as a function of increase in alkyl chain length (R) is shown in Fig. 3.11. NH_4^+ ions behave like alkali

TABLE - 3.14

Hydrated radii (r_h) and solvation layer thicknesses (t) of some alkali metal and R_4N^+ cations.

Cation	r_h / Å	**t** / Å
Li^+	3.80	3.12
Na^+	3.60	2.65
Cs^+	3.30	1.61
NH_4^+	3.31	1.83
$(CH_3)_4 N^+$	3.67	0.20
$(C_2H_5)_4 N^+$	4.00	0
$(n\text{-}C_3H_7)_4 N^+$	4.52	0
$(n\text{-}C_4H_9)_4 N^+$	4.94	0

metal counterions and their effect can be understood in the light of electrostatic interactions with anionic headgroups. For other R_4N^+ counterions, salts with less carbon number (in R) are more effective in decreasing the cmc at lower salt concentrations. On the other hand, the opposite is true at higher [salt]. At low concentration range, the electrostatic interactions seem important and, therefore, a smaller Me_4N^+ ion is more effective for cmc lowering (bulkiness of other ions keeps the positive and negative charges at relatively larger distances). With increase in the salt content, however, the situation starts changing. In addition to that of increased hydrophobic interactions (due to longer alkyl chains), other factors such as dehydration of headgroups become important. The cloud point (CP) studies on similar systems support the view point as CP was observed with Bu_4NBr and not with Me_4NBr.[24] This means that at higher [R_4NBr], the Bu_4NBr is effective due to decrease in headgroup hydration and simultaneous modification of overall hydrophobic forces. Both the effects seem responsible for the effectiveness of Bu_4NBr in decreasing cmc of SDBS at the higher salt concentrations. For other salts of the series we can expect the variation of different forces accordingly.

Figure 3.12 shows the cmc - [salt] profiles of bulky counterions (Bu_4N^+ , Bu_4P^+ or ϕ_4P^+). First, we shall consider salts with the same alkyl chain (Bu) with different connecting atoms (N or P). The data clearly suggest that Bu_4P^+ is more effective in decreasing the cmc. Presumably the larger size of the P-atom assists in decreasing the hydration of the anionic headgroups, and is thus responsible for the greater cmc decrease with Bu_4PBr. When the effects of butyl and phenyl chains with same connecting atom (P-atom) are considered, we see that the butyl chains are more effective in decreasing cmc. Aromatic additives behave differently in the

cationic than they do in the anionic surfactant systems. This ability stems from interaction of the delocalized π-electron cloud of the benzene ring[2] which may slightly hinder ϕ_4P^+ in its interaction with the DBS^-. The resulting reduction in a favorable factor for the micellization in case of ϕ_4P^+, makes it inferior in decreasing cmc in comparison to Bu_4P^+.

The α-values with different inorganic and quaternary bromides are recorded in Table 3.13. The α-values are known to depend mainly upon the electrostatic interactions of each counterion with the charged headgroups of the surfactant. Except an increase with Li^+ and a decrease with all the other counterion additions, no definite trend is found regarding α-values. This may be due to the fact that Li^+ is highly hydrated[26] and its strong interaction with anionic DBS^- takes place to a lesser extent ; this seems to be the reason for observing higher α-values. Also, Na^+ - Li^+ repulsive force may be another factor for observing the higher α-values in presence of Li^+ .

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CHAPTER IV

ROLE OF QUATERNARY BROMIDES TO CHANGE THE SOLUBILIZATION SITE OF ORGANIC COMPOUNDS IN CATIONIC MICELLAR SOLUTIONS

INTRODUCTION

On dissolution in water, surfactants form a variety of aggregates (spherical micelles, rod-shaped micelles, vesicles, etc.).[1] The driving force for the formation of aggregates is a hydrophobic attraction by the alkyl portion of the surfactant.[2] The introduction of certain organic additives can modify such forces and cause micellar growth.[3-5] It has been proposed that the interfacial partitioning of organic additives causes micellar growth, whereas their core solubilization produces swollen micelles.[6,7] Thus, knowing the location, partitioning, and orientation of organic additives in aggregated assemblies is of fundamental importance in understanding the nature of solubilization and its consequence on micellar morphology.[8-10]

Unlike homogeneous solvents, micelles possess a gamut of solubilization environments, ranging from the apolar micellar core to the relatively polar micelle-water interface.[11] Mukerjee[12] proposed that an additive which is surface active to a hydrocarbon-water interface would be solubilized mainly around the headgroup region and would promote micellar growth. The hydrophilic ranking of organic additives (e.g., alcohols or amines) by Wormuth and Kaler[13] may be viewed in terms of their partitioning behavior between micellar and aqueous *pseudo*-phases. Yamashita *et al.*[14] reported earlier that amines were solubilized in ionic micelles by electrostatic and hydrophobic effects with the amine group left on the surface .

Surfactant solutions containing spherical micelles are isotropic and their viscosities are low.[15] The presence of grown micelles in a solution causes increased viscosity because of the mutal interactions.[16,17] It was

reported earlier that viscosity increases with an increase in additive concentration and that its magnitude is substantial in the simultaneous presence of salts and organics.[7,18] It is well known that the addition of inorganic salts decreases both the electrostatic interactions between the micelles and the partitioning of organic additives between the bulk solvent and the micelles.[19] Recently, it has been shown that the polarity of the whole micelle can be tuned by the presence of a compatible additive.[10,20]

In contrast to inorganic cations (e.g., Na^+, K^+, etc.), quaternary cations (R_4M^+, M = N, or P) are essentially nonhydrated. Such salts exhibit 'salting in' effects, in contrast to the 'salting out' effects of inorganic salts.[21] Since R_4M^+ are known to modify the 3-D structure of water around them in a way similar to that of some simple short chain hydrocarbons, it could be of considerable interest to see how such salts affect the partitioning of organic additives and the resultant overall course of viscosity. Given that viscosity is sensitive to the shape and size of microscopic objects in a homogeneous suspension, one can expect evolution of the micellar shape to be reflected in a variation in viscosity.[22]

In the present work, no attempt was made to draw quantitative information out of the present viscosity data, since it is undesirable to extract size information from simple viscosity data. Hence, the effect of addition of *n*-heptylamine (C_7NH_2) on the viscosity behavior of two cationic (cetyltrimethylammonium bromide, C_{16}TAB, and tetradecyltrimethylammonium bromide, C_{14}TAB) micellar solutions containing some symmetrical/ asymmetrical quaternary bromides at different concentrations has been carried out.

RESULTS

The relative viscosity, η_r, values for 100 mM $C_{16}TAB$ with the addition of different organic additives (*n*-heptane, *n*-heptanol and *n*-heptylamine) are given in Table 4.1. Table 4.2 contains the η_r data of 100 mM $C_{16}TAB$ + 100 mM Bu_4NBr system in presence of different concentrations of the above organic compounds. The η_r data of 100 mM $C_{16}TAB$ having different fixed concentrations of Bu_4NBr and varied [*n*-heptylamine] are summarized in Table 4.3. The values of η_r of 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 system at different concentrations of KBr/quaternary ammonium bromides are recorded in Table 4.4. Table 4.5 contains η_r data of 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 in presence of different concentrations of various quaternary phosphonium bromides. The η_r values of 100 mM $C_{16}TAB$ and different fixed concentrations of C_7NH_2 with the addition of Bu_4NBr are given in Table 4.6. Effect of addition of Bu_4NBr on the viscosity of the two surfactants ($C_{14}TAB$ and $C_{16}TAB$) containing 150 mM C_7NH_2 are summarized in Table 4.7. The relevant η_r variations are shown in Figs. 4.1-4.8.

DISCUSSION

From the plots of Fig. 4.1 it can be observed that η_r of 100 mM $C_{16}TAB$ shows practically no change with *n*-heptane while a significant rise in η_r is observed with *n*-heptanol. *n*-Heptylamine seems to behave in between that of *n*-heptane and *n*-heptanol. These η_r variations with different organic additives may be due to nature of the additives and their partitioning sites in micellar systems. *n*-Heptane behaves as a hydrophobic molecule and gets solubilized in the interior of micelles. This type of solubilization can

TABLE-4.1.

Effect of addition of different organic compounds on the viscosity of 100 mM C_{16}TAB at 30 °C.

[Additive] / mM	η_r		
	n-Heptane	*n*-Heptanol	*n*-Heptylamine
0	1.35	1.35	1.35
10	1.38	1.38	-
20	1.48	1.42	-
25	-	1.54	-
30	-	1.66	1.30
35	-	1.89	-
40	1.41	2.37	-
50	1.45	4.09	-
57	(turbid)	5.98	-
60		(turbid)	1.33
80			1.34
100			1.45
130			1.80
150			2.19
170			2.38
180			3.12
190			3.42
211			4.80
212			(turbid)

TABLE-4.2.

Effect of addition of different organic compounds on the viscosity of 100 mM C_{16}TAB + 100 mM Bu_4NBr at 30 °C.

[Additive] / mM	η_r		
	n-Heptane	*n*-Heptanol	*n*-Heptylamine
0	1.29	1.29	1.29
10	1.29	-	1.33
17	-	1.35	-
20	1.31	1.37	-
30	-	1.61	1.32
36	1.30	-	-
40	(turbid)	2.42	-
49		-	1.43
50		4.29	-
55		5.52	-
63		10.38	-
90		(turbid)	2.10
100			2.29
130			3.15
140			3.31
150			3.72
176			4.93
179			(turbid)

TABLE-4.3.

Effect of addition of *n*-heptylamine (C_7NH_2) on the viscosity of 100 mM C_{16}TAB + x mM tetra-*n*-butylammonium bromide at 30 °C.

$[C_7NH_2]$ / mM	In η_r							
	x → 0.0	25	50	75	100	200	300	400
0	0.28	0.19	0.25	0.22	0.25	0.42	0.47	0.58
10	-	-	0.22	-	0.28	-	-	-
20	-	-	-	0.24	-	-	-	-
24	-	0.22	-	-	-	-	-	-
30	0.27	-	0.25	-	0.27	0.38	0.53	-
40	-	-	0.25	0.27	-	-	-	-
42	-	0.24	-	-	-	-	-	-
49	-	-	0.27	-	0.36	-	-	-
50	-	-	-	-	-	0.42	0.51	0.66
60	0.28	0.26	0.33	0.40	-	0.48	-	-
70	-	-	0.43	-	-	-	-	-
80	0.29	0.41	-	0.58	-	0.56	0.56	-
85	-	-	0.57	-	-	-	-	-
90	-	-	-	-	0.74	-	-	-
100	0.37	0.56	-	0.81	0.83	0.62	0.59	0.68
110	-	-	0.94	-	-	0.73	-	-
116	-	-	-	0.95	-	-	-	-
120	-	0.83	-	-	-	0.76	0.66	-
130	0.59	0.95	1.21	1.23	1.14	0.80	-	-
140	-	-	-	-	1.19	-	-	-
150	0.78	1.18	1.58	1.45	1.31	-	0.75	0.74
158	-	1.36	-	-	-	-	-	-
168	-	-	-	1.68	-	-	-	-
170	0.86	-	-	(turbid)	-	0.99	-	-
175	-	-	1.94		-	1.01	0.81	0.78
176	-	1.64	(tubrid)		1.59	-	-	-
180	1.14	(turbid)			-	-	-	-
190	1.23				-	-	-	-
200	-				(turbid)	1.13	0.88	0.82
211	1.57					-	-	-
221	(turbid)					1.22	-	-
250						(turbid)	1.00	0.87
254							1.06	-
300							(turbid)	0.97
350								1.02
450								1.17
452								(turbid)

TABLE-4.4.

Effect of addition of different salts on the viscosity of 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 at 30 °C.

[Salt] / mM	ln η_r				
	KBr	Pr_4NBr	Bu_4NBr	Am_4NBr	Oc_4NBr
0	0.75	0.75	0.75	0.75	0.75
0.5	-	-	-	-	0.81
1.0	-	-	-	-	0.82
1.5	-	-	-	-	0.82
2.0	-	-	-	-	0.85
2.5	-	-	-	-	0.85
3.0	-	-	-	-	0.80
3.3	-	-	-	-	0.77
4.0	-	-	-	-	0.69
4.5	-	-	-	-	0.67
5.0	0.95	-	-	-	0.77
6.0	-	-	-	-	0.55
7.0	-	-	-	-	0.47
7.5	-	-	-	0.88	-
8.0	-	-	-	-	0.41
8.7	-	-	-	-	0.41
9.0	-	-	-	-	0.41
10	1.06	-	-	-	0.39
12.5	-	-	-	0.75	(turbid)
15	1.12	-	-	-	
20	1.27	1.52	-	-	
25	-	-	1.18	0.67	
30	1.53	1.78	-	-	
35	-	-	-	0.63	
40	1.85	-	-	-	
50	1.88	2.15	1.58	0.56	
70	2.32	-	-	-	
75	-	-	1.45	0.55	
90	2.46	-	-	-	
100	-	2.24	1.31	0.52	
110	2.48	-	-	-	
130	(turbid)	-	-	-	
150		2.26	-	0.52	

Contd...

175	2.23	-	-
200	2.20	0.89	0.61
250	-	-	0.67
300	1.95	0.75	(turbid)
400	1.79	0.72	
500	1.66	-	
600	1.59	0.93	
744	1.44	-	
800	-	1.22	
1000	1.34	1.43	
1250	1.39	(turbid)	
1500	1.53		
1600	(turbid)		

TABLE-4.5.

Effect of addition of different phosphonium salts on the viscosity of 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 at 30 °C.

[Salt] / mM	ln η_r		
	ϕ_4PBr	Bu_4PBr	$Pr\phi_3PBr$
0	0.75	0.75	0.75
2.0	0.75	-	-
4.0	0.79	-	-
5.0	-	-	0.83
6.0	0.80	-	-
10	0.82	0.97	0.88
13	-	-	0.98
15	0.80	-	-
20	0.73	1.01	-
25	-	-	0.88
30	0.73	1.05	-
38	-	-	0.77
40	0.64	-	-
50	(turbid)	0.96	0.73
65		0.93	-
75		-	0.61
86		0.80	-
100		0.71	0.53
192		-	0.48
200		0.53	-
288		-	0.51
300		0.58	-
400		0.69	0.63
500		0.85	0.71
600		0.83	0.80
684		-	0.97
700		0.96	(turbid)
730		(turbid)	

TABLE-4.6.

Effect of addition of Bu_4NBr on the viscosity of 100 mM $C_{16}TAB$ + x mM C_7NH_2 at 30 °C.

[Salt] / mM	$\ln \eta_r$		
	x → 100	150	175
0	0.37	0.78	0.97
25	0.56	1.18	1.64
50	0.94	1.58	1.94
75	0.81	1.45	-
100	0.84	1.31	1.57
200	0.62	0.89	0.99
300	0.59	0.75	0.81
400	0.68	0.72	0.78
500	(turbid)	(turbid)	(turbid)

TABLE-4.7.

Effect of addition of Bu_4NBr on the viscosity of 100 mM surfactant + 150 mM C_7NH_2 at 30 °C.

[Salt] / mM	$\ln \eta_r$	
	$C_{16}TAB$	$C_{14}TAB$
0	0.78	0.80
25	1.18	-
30	-	1.37
40	-	1.38
50	1.58	1.44
70	-	1.29
75	1.45	-
100	1.31	1.15
150	-	0.89
200	0.89	0.76
300	0.75	0.68
400	0.72	0.75
600	0.93	0.93
800	1.21	1.18
990	-	1.36
1000	1.43	(turbid)
1200	(turbid)	

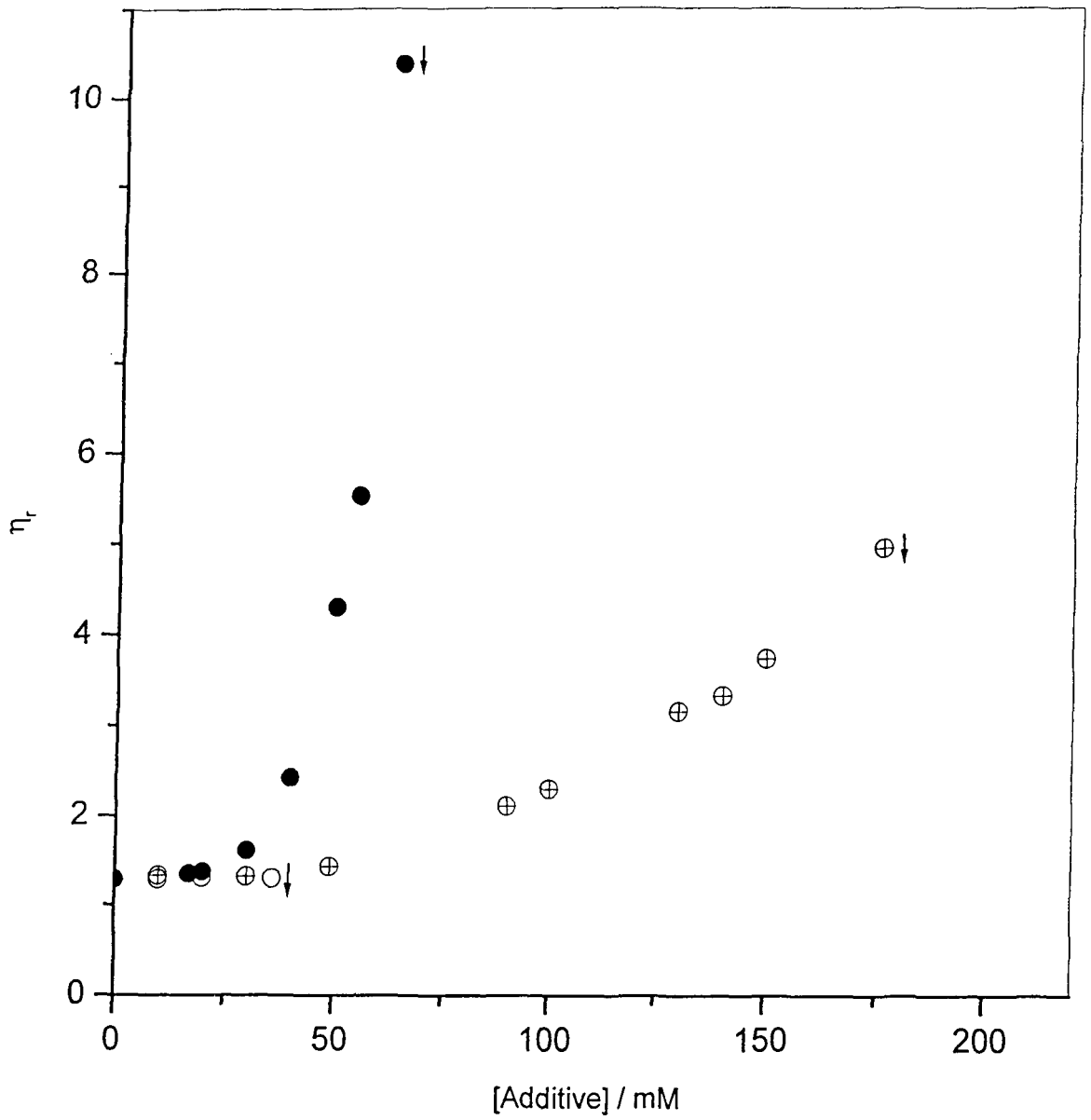

Fig. 4.1. Plots of relative viscosities (η_r) of 100 mM C_{16}TAB micellar solutions as a function of [additive] (upto the solubility limits indicated by arrows) at 30 °C : (○), *n*-heptane; (●), *n*-heptanol; (⊕), *n*-heptylamine.

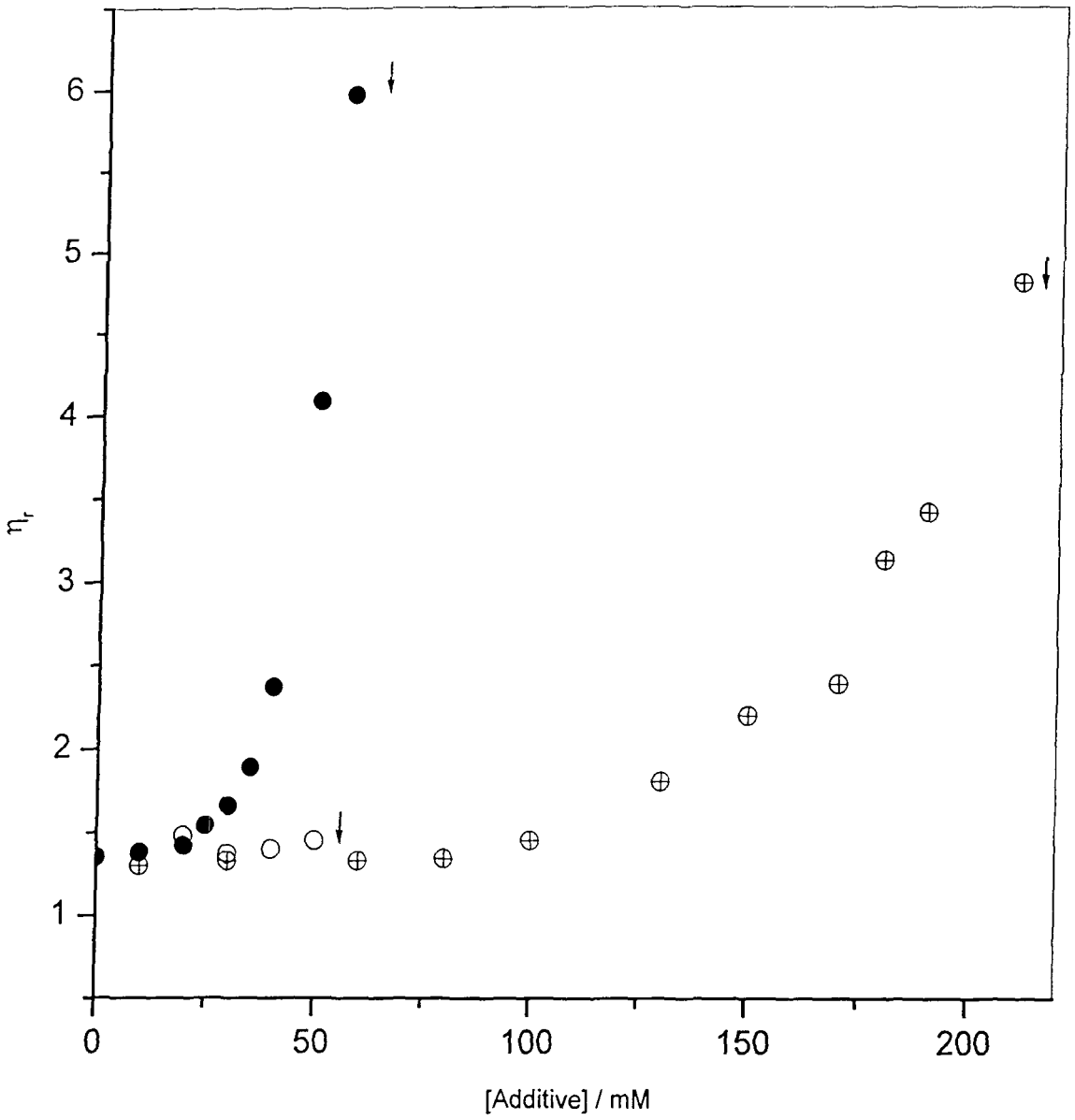

Fig. 4.2. Plots of relative viscosities (η_r) of 100 mM $C_{16}TAB$ + 100 mM Bu_4NBr micellar solutions as a function of [additive] (upto the solubility limits indicated by arrows) at 30 °C : (○), *n*-heptane; (●), *n*-heptanol; (⊕), *n*-heptylamine.

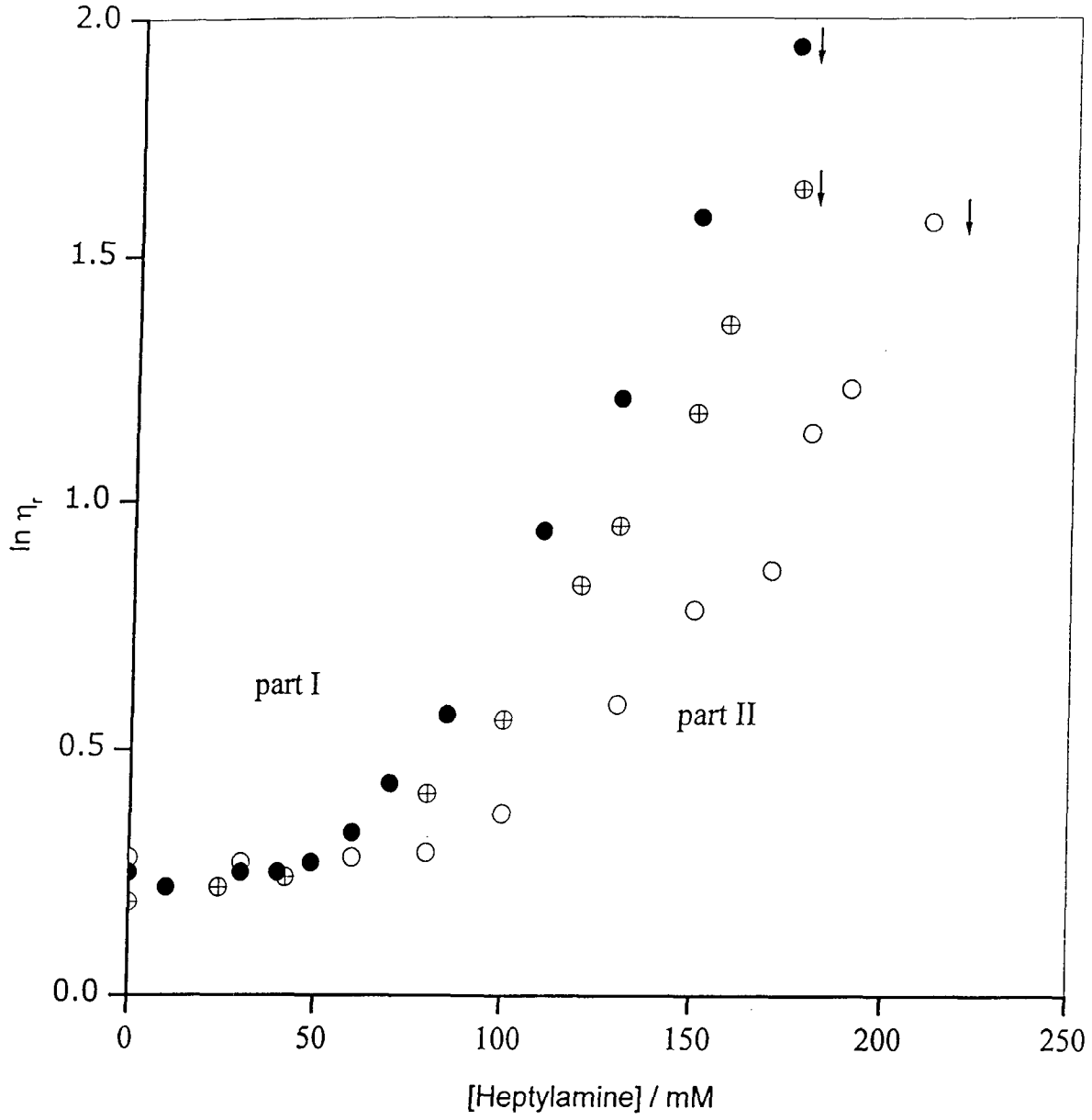

Fig. 4.3. Plots of relative viscosities (η_r) of 100 mM $C_{16}TAB$ micellar solutions as a function of added *n*-heptylamine (upto the solubility limits indicated by arrows) at various fixed (lower) concentrations (x) of Bu_4NBr at 30 °C : x = 0.0, (○); 25, (⊕); 50 mM, (●).

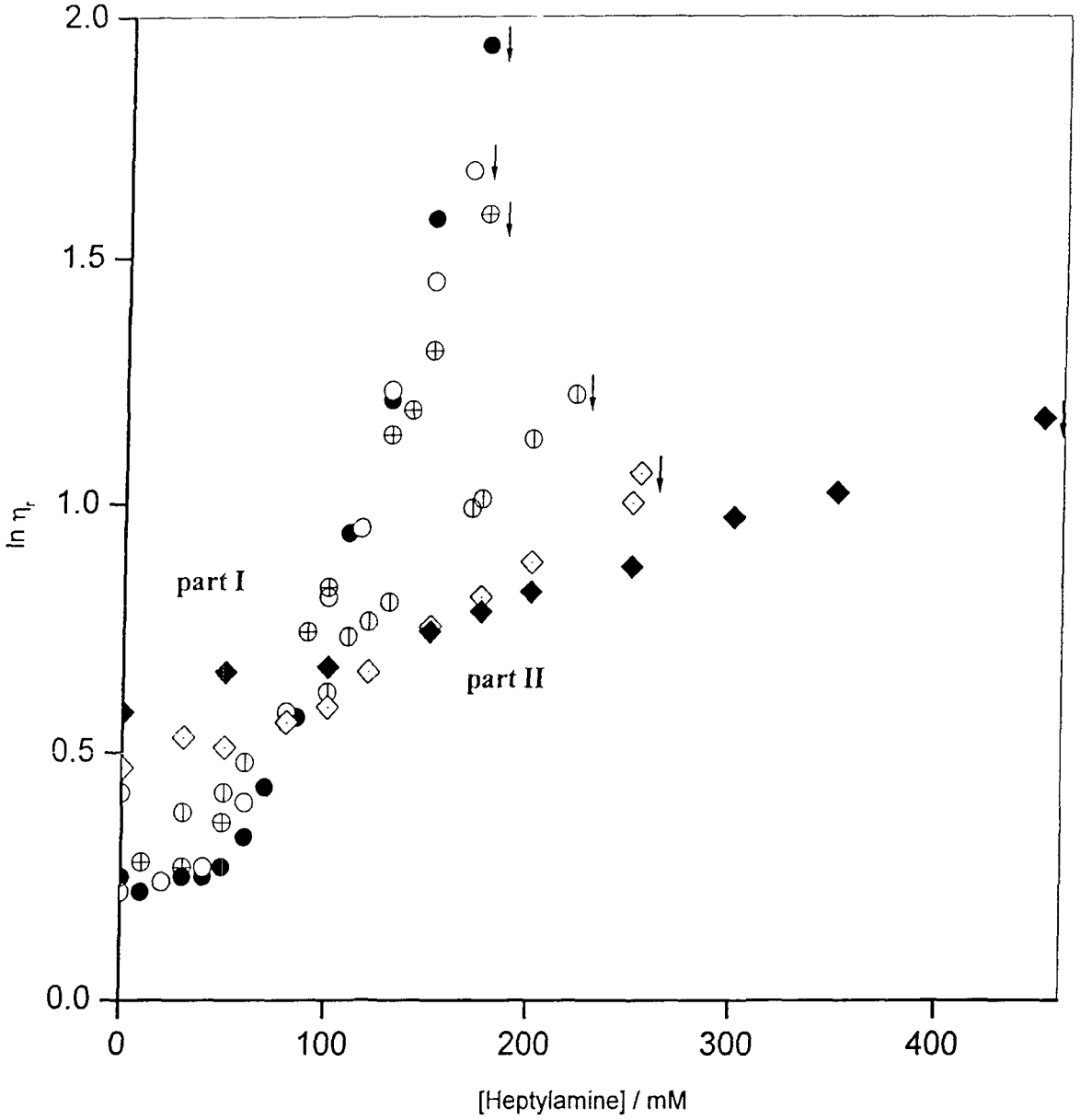

Fig. 4.4. Plots of relative viscosities (η_r) of 100 mM $C_{16}TAB$ micellar solutions as a function of added *n*-heptylamine (upto the solubility limits indicated by arrows) at various fixed (higher) concentrations (x) of Bu_4NBr at 30 °C : x = 50, (●); 75,(○); 100, (⊕); 200, (◐); 300, (◇); 400 mM, (◆).

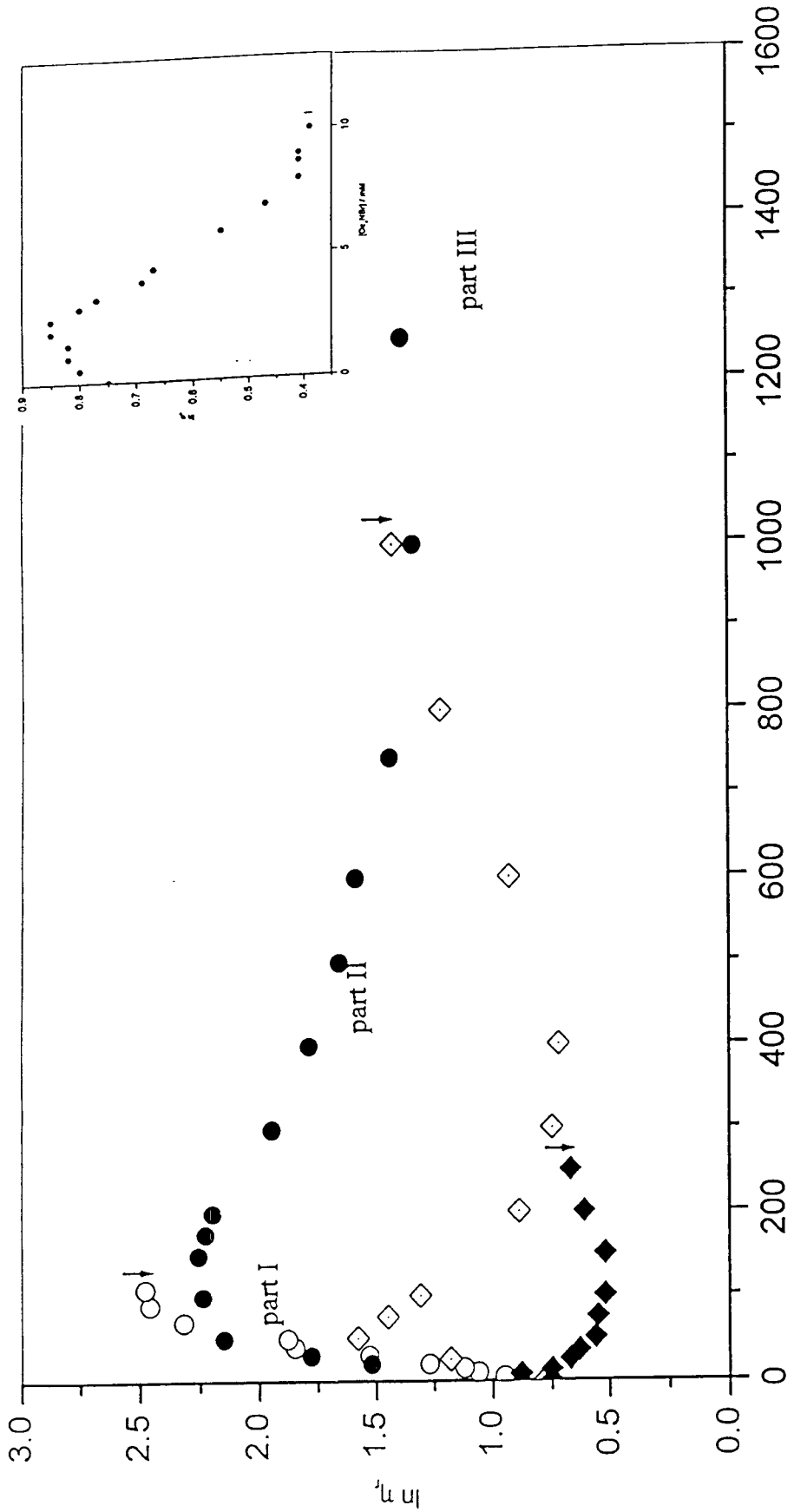

Fig. 4.5. Plots of relative viscosities (η_r) of 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 (*n*-heptylamine) micellar solutions as a function of added salts (upto the solubility limits indicated by arrows) at 30 °C : (○), KBr; (●), Pr_4NBr; (◇), Bu_4NBr; (◆), Am_4NBr; (⬢), Oc_4NBr (shown in inset).

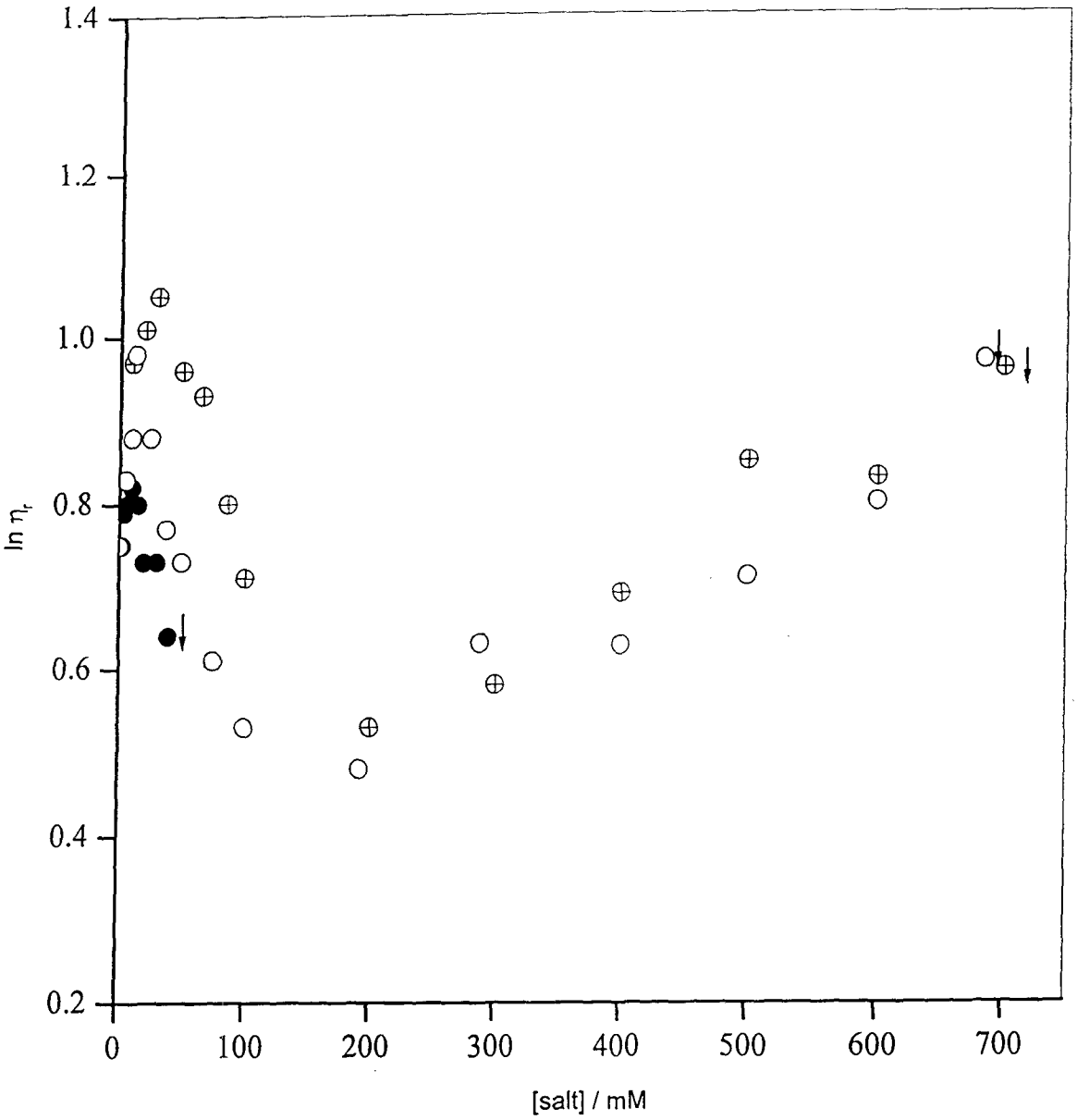

Fig. 4.6. Plots of relative viscosities (η_r) of 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 (*n*-heptylamine) micellar solutions as a function of added phosphonium salts (upto the solubility limits indicated by arrows) at 30 °C : (●), ϕ_4PBr; (⊕), Bu_4PBr; (○), $Pr\phi_3PBr$.

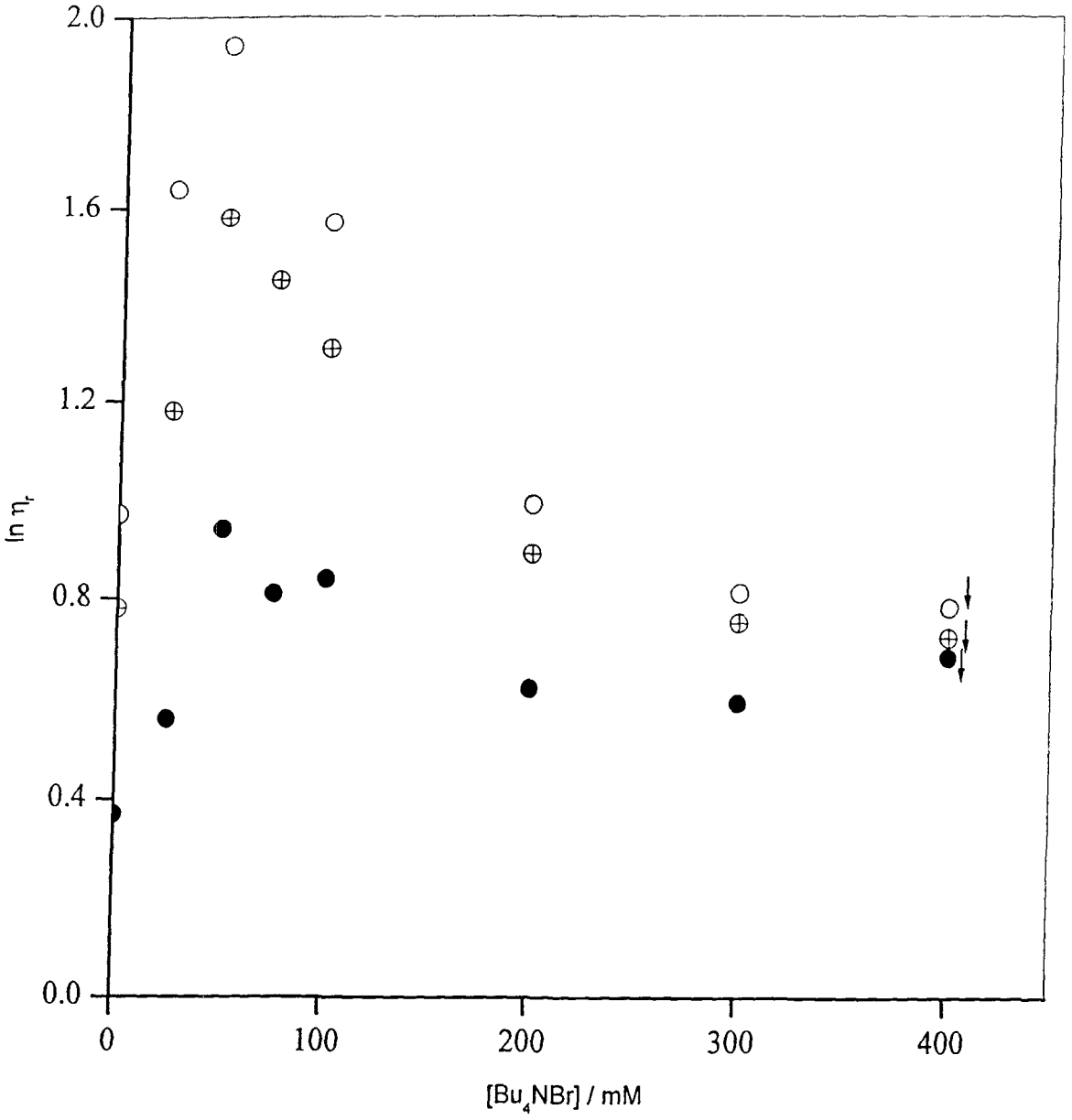

Fig. 4.7. Plots of relative viscosities (η_r) of 100 mM $C_{16}TAB$ micellar solutions as a function of added Bu_4NBr (upto the solubility limits indicated by arrows) at various fixed concentrations (x) of *n*-C_7NH_2 at 30 °C : 100, (●); 150, (⊕); 175 mM (○).

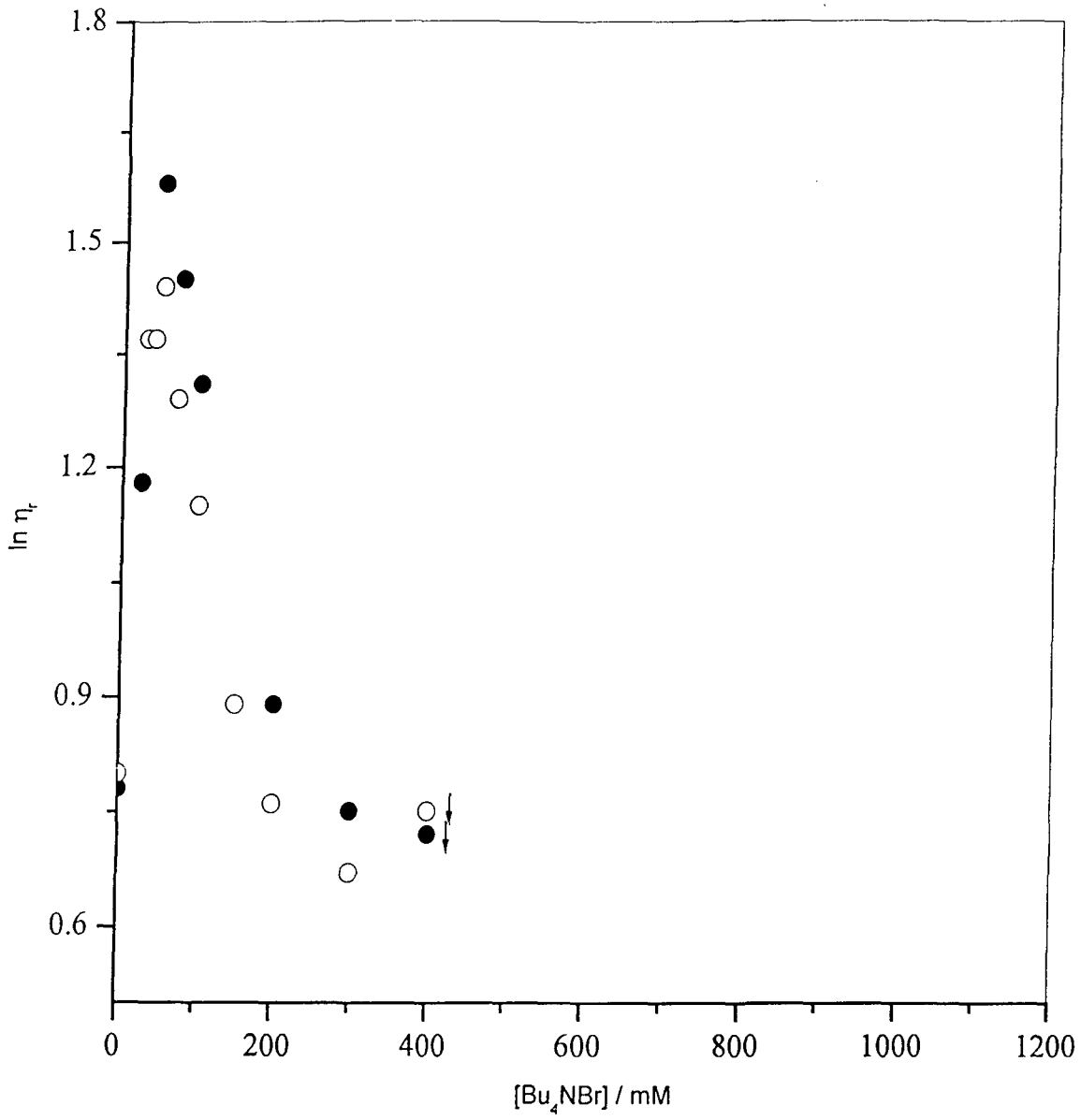

Fig. 4.8. Plots of relative viscosities (η_r) of 100 mM surfactant + 150 mM C_7NH_2 (*n*-heptylamine) as a function of added Bu_4NBr (upto the solubility limits indicated by arrows) at 30 °C : (○), $C_{14}TAB$; (●), $C_{16}TAB$.

produce slightly swollen micelle but does not affect much the size of the micelle[10,23] and hence no significant change in viscosity was observed with *n*-heptane (Fig. 4.1). Due to the presence of hydrophilic group (–OH or –NH_2) in *n*-heptanol or *n*-heptylamine, the additive can partition in the micellar headgroup region. The partitioning of different organic compounds and their possible effects on micellar morphology are discussed by Lindemuth and Bertrand.[3] It is reported that additive partitioning at the interfacial region depends upon the nature of charge of the micelle and the functional group present in the organic additive. The partitioning of an additive in the interfacial region of the micelle causes charge shielding while their alkyl chains can increase hydrophobic interactions. These two simultaneous effects cause micelles to grow with the concomitant increase in η_r. This indeed was observed with *n*-heptanol and *n*-heptylamine (Fig. 4.1).

Figure 4.2 shows the variation of η_r with different additive concentrations added to 100 mM C_{16}TAB + 100 mM Bu_4NBr solutions. Here again η_r does not show any significant change with *n*-heptane while *n*-heptanol and *n*-heptylamine show similar behavior as in Fig. 4.1. The overall viscosity behavior could be understood in the light of discussion made in the above paragraph. Though both the headgroup-region-partitioned compounds (*n*-heptanol and *n*-heptylamine) are potential candidates, *n*-heptylamine (C_7NH_2) was chosen for making detailed studies due to wider solubility window (Figs. 4.1 and 4.2).

Figure 4.3 shows the relative viscosities of different C_7NH_2 contents added to 100 mM C_{16}TAB solutions containing various fixed amounts of Bu_4NBr at 30 °C. Owing to its amphiphilic nature,[3] C_7NH_2 partitioned

mainly in the headgroup region, with the result that hydrophobic interactions increased and the Mitchell-Ninham parameter (R_p) was modified.[24] Fang and Venable[25] used this packing ratio to explain different structural transitions. One can see that without Bu_4NBr, a gradual addition of C_7NH_2 in pure 100 mM $C_{16}TAB$ caused no change in viscosity at lower [C_7NH_2] (part I, Fig. 4.3) and that a distinct rise was observed at higher [C_7NH_2] (part II, Fig. 4.3). This viscosity increase was due to the micellar growth which was the result of a modification in the R_p. These data are in agreement with earlier works.[5,7,18] Similar experiments carried out with some lower [Bu_4NBr] showed that in presence of the salt, the viscosity increase commenced at lower [C_7NH_2] and also that $|\eta_r|$ was higher in comparison with no salt. This may be due to a synergistic effect of the Br^- (produced from Bu_4NBr) and C_7NH_2 present simultaneously in the system, as the former causes charge shielding among the micelles, whereas the alkyl chains of C_7NH_2 increase hydrophobic interactions.

Figure 4.4 shows the $\eta_r - [C_7NH_2]$ plots for 100 mM $C_{16}TAB$ solutions containing higher [Bu_4NBr]. The viscosity pattern in part I is more or less similar to that shown in Fig. 4.3, but one can observe an unexpected systematic decrease in viscosity with increasing [Bu_4NBr] in part II. Undoubtedly, the systems in part II had higher [Bu_4NBr] as well as [C_7NH_2]; therefore, more Br^- and C_7NH_2 contents were available to produce micellar growth, and a consequent rise in viscosity was expected. In reality, this was not the case, instead, we saw a fall in viscosity (Fig. 4.4). Regarding the reasons for the changed behavior, the key probably lay in a change in the site of solubilization at higher salt contents : C_7NH_2 no longer went to the

interfacial region, the conventional site. Hence, the reasons of decrease in viscosity were investigated by examining the role of Bu_4N^+ in the present context. In this ion, four butyl chains surround the positive charge on the N-atom. The positive charge on the $C_{16}TAB$ micelles would cause Bu_4N^+ ions to remain in the bulk solution. These Bu_4N^+ may create apolar centers (cavities) in the background solution wherein C_7NH_2 become solubilized (a change in the site of solubilization). If this were the case then the effective C_7NH_2 content at the interfacial region would be reduced, with concomitant decreases in both hydrophobic interactions and consequent micellar growth. This decreased micellar growth would impart less viscosity to the solution and be the reason for the kind of behavior observed in part II of Fig. 4.4. The increase in aqueous solubility of hydrocarbons in the presence of such salts (e.g., Bu_4NBr) has been explained earlier on the basis of the incorporation of hydrocarbon molecules into holes in the icelike framework of water molecules.[5,26] In the present context, this tendency seemed to predominate, as indicated by the overall pattern of viscosity.

To support the viewpoint, viscosity measurements were performed on 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 systems with varying concentrations of different quaternary salts (Fig. 4.5). For purposes of comparison, similar viscosity measurements were made with KBr, and a continuous increase in η_r was observed with the progressive addition of the salt. In contrast, with R_4N salts the viscosity increased (part I), decreased (part II), and increased again (part III). This behavior is new but akin to that observed with Na salts of organic acids,[27,28] which have an altogether different origin.[29] With KBr, the continuous viscosity increase may be due to the synergistic effect of Br^-

and C_7NH_2 (as discussed in the previous paragraph). That no viscosity decrease occurred suggests that the site of solubilization of C_7NH_2 did not change with the presence of KBr. The presence of any of the quaternary ammonium bromides (R_4NBr) resulted in a change in behavior, and the appearance of a peak simply suggests that a depletion in synergism took place after the peak. We can also see that the peak position shifted to lower [salt] as the length of R-part of the salt increased in the system. Furthermore, the second viscosity-increasing region is also diminished. As mentioned earlier, these salts cause C_7NH_2 to withdraw from the interfacial region. This effect is very well corroborated with the results depicted in Fig. 4.5 : we see that longer the R-part of the salt, lower is the [salt] required to produce the peak with a progressively lowering $|\eta_r|$. Obviously, longer chains can initiate a change in the site of solubilization at lower [salt]. The second region where a viscosity increase was observed at higher [salt] seemed to be related to the presence of a higher Br^- content which simply reduced the intermicellar / intramicellar electrical repulsion and caused micellar growth. Regarding the role of C_7NH_2 in this range, its concentration remained constant, thus, the micellar interfacial region was no longer depleted and had less significance toward the overall viscosity of the system. The absence of the second region of increasing viscosity with Oc_4NBr was due to the fact that the overall salt content in the system was comparatively small (instability of the solution hampered experimentation at higher [salt]), which gave a lower number of Br^- (insufficient to increase micellar growth). One more point worth noting is that the length of the alkyl part of the R_4N salt seemed to play more significant role than salt

concentration, because significantly less Oc_4NBr, for example, was effective in initiating the behavior.

Figure 4.6 shows the effect of adding symmetrical or asymmetrical quaternary phosphonium bromides (Bu_4PBr, ϕ_4PBr, or $Pr\phi_3PBr$) in the 100 mM $C_{16}TAB$ + 150 mM C_7NH_2 solutions. A point worth noting is that with Bu_4PBr, the peak appeared at a lower concentration than with Bu_4NBr. This may be because the the size of Bu_4P^+ is bigger than Bu_4N^+; therefore, Bu_4P^+cavities could accommodate a larger volume of C_7NH_2 at the same [salt] and be responsible for the effect appearing earlier than with Bu_4NBr. Solubilities of phenyl salts were considerably lower; however, the effect began to appear early with these salts, with the absence of a second region of increasing viscosity. This may again be due to the larger size of the phenyl salts (compared with Bu_4PBr), which were responsible for initiating the effect at lower [salt]. We see that $Pr\phi_3PBr$ (where one phenyl ring is replaced by a propyl chain) shifted the initiation of the effect to higher [salt] because the size of the $Pr\phi_3P^+$ is slightly lower than ϕ_4P^+.

Figure 4.7 shows the variation in η_r with [Bu_4NBr] observed with 100 mM $C_{16}TAB$ containing different fixed [C_7NH_2]. Perusal of the data shows that $|\eta_r|$ was dependent on the [C_7NH_2] but the [salt] at which peaks appeared was more or less the same in all the systems. This indicates that a minimum concentration of salt, independent of the additive content in the system, is needed to initiate the peaked behavior. The $|\eta_r|$ of the system containing higher [C_7NH_2] was as expected due to a partitioning of C_7NH_2 between the interfacial region and the bulk solution (because of the presence of Bu_4NBr). Since the total C_7NH_2 content was higher, the interfacial

content was also higher and was responsible for the synergism with higher η_r values. Other features of Fig. 4.7 are similar and can be understood on the basis of reasoning presented in the earlier part of the paper.

Figure 4.8 shows the effect of chain length of the surfactant present in the system. The behavior of the two surfactants used ($C_{14}TAB$ or $C_{16}TAB$) was similar and the η_r^{max} was obtained at the same [Bu_4NBr] but with a different magnitude. This suggests that the chain length of the surfactant had little effect on the [salt] at which the peaked behavior appeared. However, the higher-chain-length surfactant ($C_{16}TAB$) produced a more viscous system than its lower-chain-length counterpart ($C_{14}TAB$). Although the contents of the salt and C_7NH_2 present in both systems were the same, the difference observed in the magnitude of the viscosity was because $C_{16}TAB$ produced longer micelles than $C_{14}TAB$ (as the former has a higher R_p value).[24]

It can be concluded that with the addition of quaternary bromide, the site of C_7NH_2 solubilization in a cationic surfactant can be changed from the interfacial region to the background solution. This change depends on the length of the alkyl chain present in the quaternary salt. Also, the connecting atom (N or P) in the salt has a role to play. The phenyl ring seems more effective than alkyl chain of a particular salt in bringing about this shift. The chain length of the surfactant and content of additive have little effect on the [salt] at which the change in the site of solubilization commences.

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CHAPTER V

QUATERNARY SALTS AS SOLUBILIZATION SITE MODIFIERS OF ORGANIC COMPOUNDS IN ANIONIC MICELLAR SOLUTIONS

INTRODUCTION

Dilute aqueous solutions of ionic surfactants behave as strong electrolytes. At higher concentrations, however, they no more show the ideal behavior but form dynamic aggregates, i.e., spherical micelles,[1] which change some of the physical properties of the solution. These micelles can transform to rodlike or threadlike (wormlike) micelles[2] at still higher concentrations and/or when a second oppositely charged surfactant, organic/ inorganic counterion, or an uncharged cosurfactant is added.[3]

Surfactant solutions containing spherical micelles are isotropic and of low viscosity.[4] The presence of long rod-shaped micelles in the solution imparts higher viscosity to the solution.[5] There are many factors, including the nature and the concentration of the additive(s), that determine the shape of micelles. Such additives can be used to tune different intra- and inter-micellar forces and the effective packing parameter.[6]

Aqueous micelles are capable of solubilizing a certain amount of organic molecules with quite distinct polarities/hydrophobicities.[7] Unlike homogeneous solvents, micelles possess a range of solubilization environments, ranging from the nonpolar hydrocarbon core of the micelle to the relatively polar micelle-water interface.[8] The amount and the solubilization environment can play important roles in the resultant micellar morphology and viscosity of the solution. It is known that presence of inorganic counterions decreases both the electrostatic interactions between micelles and the partitioning of organic additives between micelles and bulk solvent.[9]

In view of the well-known fact that viscosity is sensitive to morphology of the microscopic objects in the solution, one can expect the evolution of the micellar morphology to be signalled in the viscosity variation.[10] Quantitative interpretation of the viscosity data is, however, outside the scope of the present work since it is undesirable to extract size parameters from simple viscosity results.

The reduction of the headgroup repulsions of micellized surfactants by counterions is an important aspect for micellar shape/size. The distribution of counterions in the vicinity of charged micelles usually has been described by Poisson-Boltzmann theory.[11] However, if interactions between counterions (hydrophobic in nature) and micelles of non-electrostatical origin, i.e., specific counterion effects, are taken into account, the theory requires further treatment. The surface charge densities of micelles formed in the presence of hydrophobic counterions are lower as compared to micelles formed by surfactants with inorganic counterions.[12] Quaternary ammonium bromides (R_4NBr) ionize like ordinary inorganic salts and give hydrophobic counterions enabling them to interact with micelles. In R_4N^+counterions which are less hydrated the single positive charge is burried in a paraffin shell and exhibit an ambivalent nature. As such counterions can interact electrostatically and hydrophobically with anionic micelles in solution, the alkyl chains of R_4N^+ may get embedded between monomers of the anionic micelle due to the hydrophobic effect. But the geometric constraints make it difficult, the result being that two directions may be chosen for bending: one is toward the water phase and the other penetrating toward the micellar interior.[13-15] The alkyl chains pointing

toward bulk water may produce a temporary hydrophobic region around the micellar surface.[16,17] In this regard it could be recalled that the presence of R_4NBr salts has been found to change the partitioning behavior of organic compounds in cationic micelles from the interfacial region to the bulk aqueous phase.[18]

On account of basicity and phase data the following rank ordering of headgroups with respect to their relative hydrophilicity is given.[19]

$$-COO^- >> -SO_3^- > -OSO_3^-$$

The structural differences in the surfactant headgroups of sodium dodecylbenzenesulfonate (SDBS) and sodium dodecylsulfate (SDS) affect their critical micellar concentrations (cmc), apparent degree of counterion dissociation (α), and clouding behavior.[19] The difference in the two surfactants is that SDBS has a phenyl ring while SDS has –O– only. This difference could be responsible for greater hydrophobic interaction between the benzene ring of the SDBS molecule and the alkyl/phenyl chains/rings of quaternary bromides. The SDBS molecule could be of considerable interest since it contains a phenyl ring between a hydrophobic chain and polar head ($-SO_3^-$). In micelles, aromatic hydrocarbons are known to have strong tendency to be located near the surface.[20] Viscosity measurements were performed under Newtonian flow conditions to see the effect of addition of quaternary bromides to SDBS micellar solutions at 30 °C. Viscosity measurements with NaBr were also made for comparison. The addition of cyclohexanol, cyclo-C_6OH, and cyclohexylamine, cyclo-C_6NH_2, to 50 mM SDBS micellar solutions with or without Bu_4NBr has been seen to affect the role of the salt as solubilization site modifier.

RESULTS

The relative viscosity, η_r, values of different concentrations of SDBS solutions are given in Table 5.1. The η_r values of 50 mM SDBS with different concentrations of added NaBr are also included in Table 5.1. Table 5.2 contains the η_r data of solutions containing different fixed concentrations of SDBS in presence of added Bu_4NBr. The η_r values of 50 mM SDBS solutions at varied concentrations of added quaternary bromides are summarized in Table 5.3. Tables 5.4 - 5.7 contain η_r data of 50 mM SDBS + different fixed concentrations of Bu_4NBr in presence of various organic additives (cyclohexane, cyclohexanol, cyclohexylamine and aniline). The corresponding η_r variations are shown in Figs. 5.1 - 5.7.

DISCUSSION

Figure 5.1 shows the variation of relative viscosity (η_r) with SDBS concentration. The sharp increase in η_r beyond certain [SDBS] suggests formation of non-spherical micelles.[3,4,21] Figure 5.1 also shows the effect of addition of NaBr on η_r of 50 mM SDBS solution (a 50 mM SDBS solution was selected because it has low viscosity and probably has spherical micelles in solution). The NaBr addition plot clearly demonstrates a sharp increase in η_r after $\simeq$ 200 mM NaBr, which suggests that NaBr addition causes micellar growth (sphere-to-rod transition, i.e., s$\rightarrow$ r). This is because the addition of salt (counterion Na^+ in this case) reduces the electrostatic repulsion between SDBS headgroups and increases the aggregation number, thus promoting micellar growth (or rod formation).

Figure 5.2 shows the variation of η_r of SDBS solutions (various fixed concentrations) with addition of Bu_4NBr. It is clear that η_r starts increasing

TABLE-5.1.

Effect of [SDBS] or [NaBr] (added to 50 mM SDBS) on the viscosity of aqueous SDBS micellar solutions at 30 °C.

	ln ηr	
Concentration / mM	SDBS	NaBr
0	-	0.10
25	0.05	-
33	-	0.08
50	0.11	-
66	-	0.86
75	0.16	-
100	0.21	0.14
125	0.25	-
133	-	0.14
150	0.29	-
166	-	0.16
200	0.44	0.23
233	-	0.33
250	0.70	-
266	-	0.50
300	1.16	0.78
317	-	0.81
330	-	1.29
350	1.34	-
400	1.85	-
450	2.58	-
500	3.40	-

TABLE-5.2.

Effect of addition of Bu_4NBr on the viscosity of x mM SDBS solutions at 30 °C.

$[Bu_4NBr]$ / mM	$\ln \eta_r$		
	x → 25	50	100
0.0	0.06	0.12	0.22
2.5	-	-	0.22
5.0	0.06	0.12	0.22
7.5	0.11	-	0.24
10	0.08	0.12	0.26
13	0.17	-	0.29
15	0.26	0.27	0.31
18	-	-	0.38
20	0.53	0.60	0.49
25	0.86	1.23	0.72
30	1.12	2.01	1.28
35	(turbid)	2.53	1.86
37		(turbid)	2.31
40			3.12
43			(turbid)

TABLE-5.3.

Effect of addition of quaternary salts on the viscosity of 50 mM SDBS solutions at 30 °C.

[Salt]/ mM	η_r				
	Bu_4NBr	ϕ_4PBr	Bu_4PBr	$Pr\phi_3PBr$	Am_4NBr
0.0	1.12	2.12	3.12	4.12	5.12
2.0	-	-	3.12	-	-
2.5	1.13	2.16	-	4.13	5.10
4.0	-	-	3.12	-	-
5.0	1.13	2.16	-	4.12	5.11
6.0	-	-	3.14	-	5.13
7.5	-	2.14	-	4.16	5.11
8.0	-	-	3.13	-	(turbid)
9.0	-	-	3.17	-	
9.6	-	-	3.16	-	
10	1.12	2.20	3.17	4.18	
11	-	-	3.19	-	
13	-	2.20	(turbid)	4.19	
15	1.30	2.20		4.24	
18	-	-		4.27	
20	1.83	2.31		4.39	
23	-	-		4.49	
25	3.36	2.35		4.63	
28	-	2.44		4.83	
30	7.49	2.45		4.94	
33	-	2.51		5.14	
35	12.55	(turbid)		(turbid)	
36	(turbid)				

TABLE-5.4.

Effect of addition of cyclohexane on the viscosity of 50 mM SDBS + x mM Bu_4NBr at 30 °C.

[Cyclohexane] / mM	η_r		
	x→0.0	15	30
0.0	1.12	1.21	5.05
0.1	1.12	-	-
0.3	1.14	-	-
0.5	1.14	-	4.90
0.6	-	-	5.18
0.7	-	-	5.34
0.8	1.13	-	-
1.0	1.13	-	5.51
2.0	1.13	-	5.75
3.0	1.12	-	6.25
3.9	-	-	6.31
5.0	1.13	-	6.38
6.0	-	-	6.40
7.0	1.14	-	6.93
7.6	-	-	7.54
8.0	-	1.15	(turbid)
10	1.13	-	
16	-	1.21	
20	1.14	-	
24	-	1.18	
30	1.14	-	
32	-	1.24	
41	1.15	-	
48	-	1.20	
50	1.16	-	
59	1.22	-	
64	-	1.20	
67	1.23	-	
80	(turbid)	1.18	
96		1.16	
112		1.21	
128		1.48	
145		1.18	
149		(turbid)	

TABLE-5.5.

Effect of addition of cyclohexanol on the viscosity of 50 mM SDBS + x mM Bu_4NBr at 30 °C.

[Cyclohexanol] / mM	η_r				
	x→0.0	10	15	25	30
0.0	1.12	1.14	1.21	2.53	5.05
0.5	-	-	-	2.44	-
1.0	-	-	-	2.44	5.07
2.0	-	-	1.23	-	5.34
2.9	-	-	-	2.40	-
3.0	-	-	-	-	5.50
4.0	-	-	-	-	5.47
4.8	-	1.13	-	-	-
5.0	-	-	-	2.42	5.39
5.6	-	-	-	2.45	-
6.0	-	-	1.26	-	5.31
6.9	-	-	-	2.48	-
7.0	-	-	-	-	5.40
8.0	-	-	-	2.49	5.42
9.0	-	-	-	2.49	-
9.7	-	-	-	-	5.32
10	1.17	-	1.20	2.47	(turbid)
12	-	1.39	-	-	
14	-	-	1.23	-	
16	-	-	-	2.42	
20	1.17	1.14	-	(turbid)	
24	-	1.15	1.25		
26	-	-	1.24		
28	-	1.15	-		
30	1.16	-	-		
32	-	1.16	-		
38	-	1.14	1.21		
43	-	1.16	1.22		
44	-	-	1.22		
45	1.16	-	-		
48	-	1.16	1.21		
52	-	-	1.20		
56	-	1.17	1.20		

Contd...

60	1.17	-	1.22
64	-	-	1.23
68	-	1.16	(turbid)
75	1.19	-	
80	1.16	1.16	
92	-	1.17	
108	-	1.18	
126	1.19	-	
129	(turbid)	1.19	
132		(turbid)	

TABLE-5.6.

Effect of addition of cyclohexylamine on the viscosity of 50 mM SDBS + x mM Bu_4NBr at 30 °C.

[Cyclohexylamine] / mM	η_r				
	x→0.0	10	15	25	30
0.0	1.12	1.14	1.21	2.53	5.05
0.3	-	-	-	2.58	5.95
0.5	-	-	1.24	2.69	6.34
0.8	-	-	-	2.91	7.45
1.0	1.12	1.16	1.34	3.19	8.21
1.5	-	-	-	3.42	10.37
2.0	1.12	-	1.37	4.16	11.14
2.5	-	-	-	4.36	11.23
2.6	-	1.17	-	-	10.96
3.0	1.30	-	1.42	4.39	(turbid)
3.5	-	-	-	4.58	
3.8	-	-	-	4.70	
4.0	1.30	1.20	1.47	-	
4.1	-	-	-	4.35	
5.0	1.12	1.19	1.87	(turbid)	
6.0	1.30	1.20	1.63		
7.0	1.12	1.24	1.73		
8.0	1.14	1.28	1.89		
9.0	-	1.30	-		
10	1.19	1.34	1.87		
12	-	1.40	1.77		
14	1.20	-	1.62		
15	-	1.30	(turbid)		
16	1.22	(turbid)			
16.2	(turbid)				

TABLE-5.7.

Effect of addition of aniline on the viscosity of 50 mM SDBS + x mM Bu_4NBr at 30 °C.

[Aniline]/ mM	η_r				
	x→0.0	10	15	25	30
0.0	1.12	1.14	1.21	2.53	5.05
0.1	-	-	-	-	5.17
0.25	1.12	-	-	-	-
0.3	-	-	-	2.53	5.21
0.5	1.12	-	-	-	5.45
0.6	-	-	-	2.53	5.59
0.7	-	-	-	-	5.66
0.75	1.12	-	-	-	-
0.8	-	-	-	2.53	5.75
0.9	-	-	-	2.53	-
1.0	1.12	-	-	2.53	5.76
1.5	-	-	-	2.52	-
1.8	-	-	-	2.51	-
2.0	1.12	1.14	-	-	5.77
2.5	-	-	-	2.54	-
3.0	1.13	-	-	-	6.06
4.0	-	1.14	-	-	6.28
5.0	1.14	-	-	2.55	6.63
6.0	-	1.14	-	-	6.85
7.0	1.14	-	-	-	6.99
7.5	-	-	-	2.59	-
8.0	-	1.16	1.22	-	7.30
9.0	-	1.16	-	-	7.55
10	1.14	1.17	-	2.70	7.61
12	-	-	1.25	-	9.68
15	-	-	-	3.02	(turbid)
16	-	-	1.27	-	
18	-	-	-	3.28	
19.6	-	-	-	3.04	
20	1.14	1.17	1.26	(turbid)	
24	-	-	1.25		
28	-	-	1.32		
30	1.16	1.18	-		

Contd...

35	-	-	1.29
40	1.17	1.19	1.32
44	-	-	1.32
48	-	-	1.34
50	1.17	1.20	-
52	-	-	1.36
54	-	-	1.31
56	-	-	1.33
58	-	-	1.33
60	-	1.22	(turbid)
70	1.20	1.24	
80	1.20	1.26	
100	1.20	1.30	
120	-	1.31	
150	1.20	(turbid)	
200	1.20		
250	1.20		
300	1.22		
342	1.22		
400	1.24		
427	1.26		
430	(turbid)		

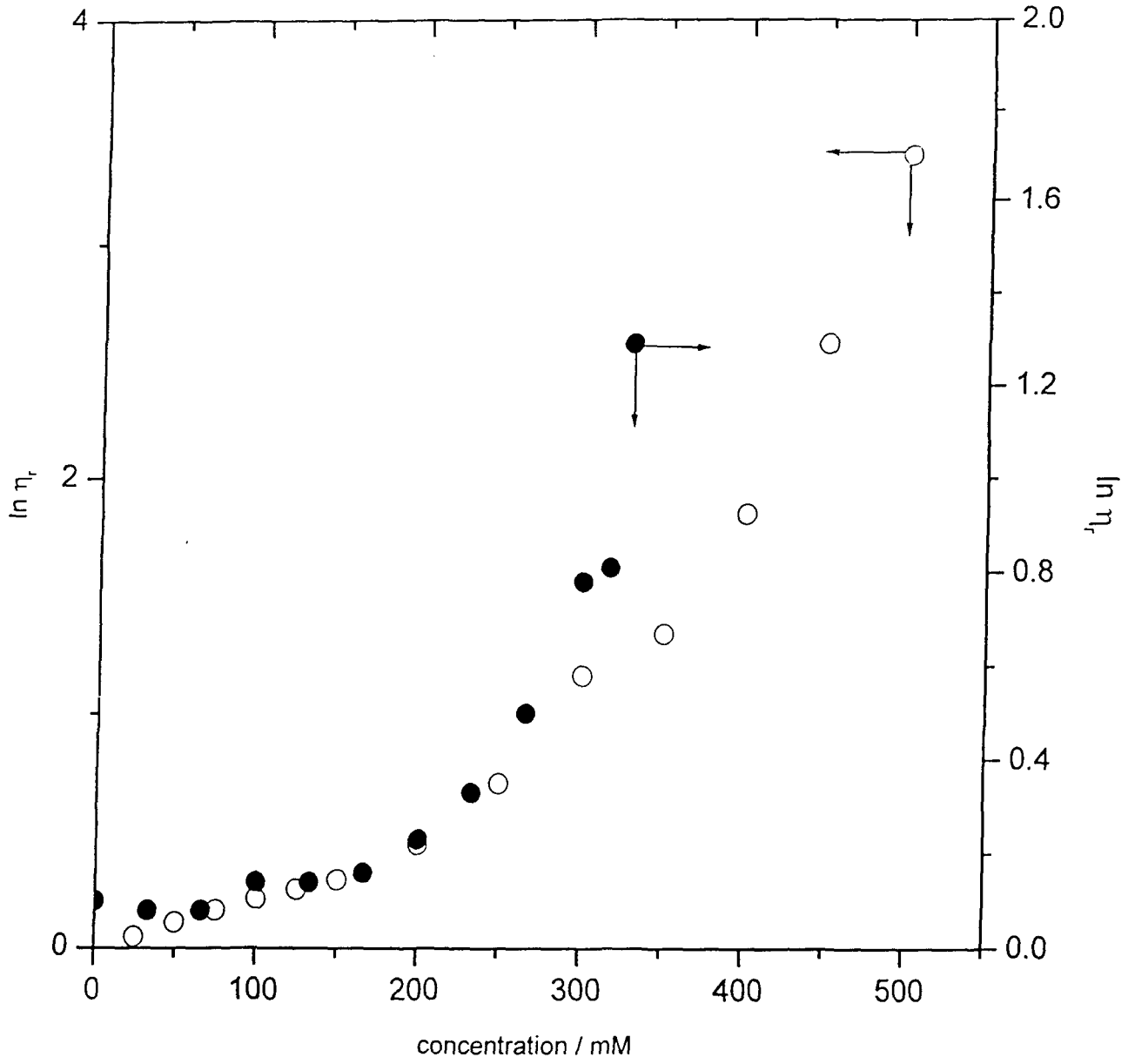

Fig. 5.1. Plots of relative viscosities (η_r) at 30 °C with the increase in concentration of sodium dodecylbenzenesulfonate (SDBS) (○) and with the addition of NaBr (●) to 50 mM SDBS solution.

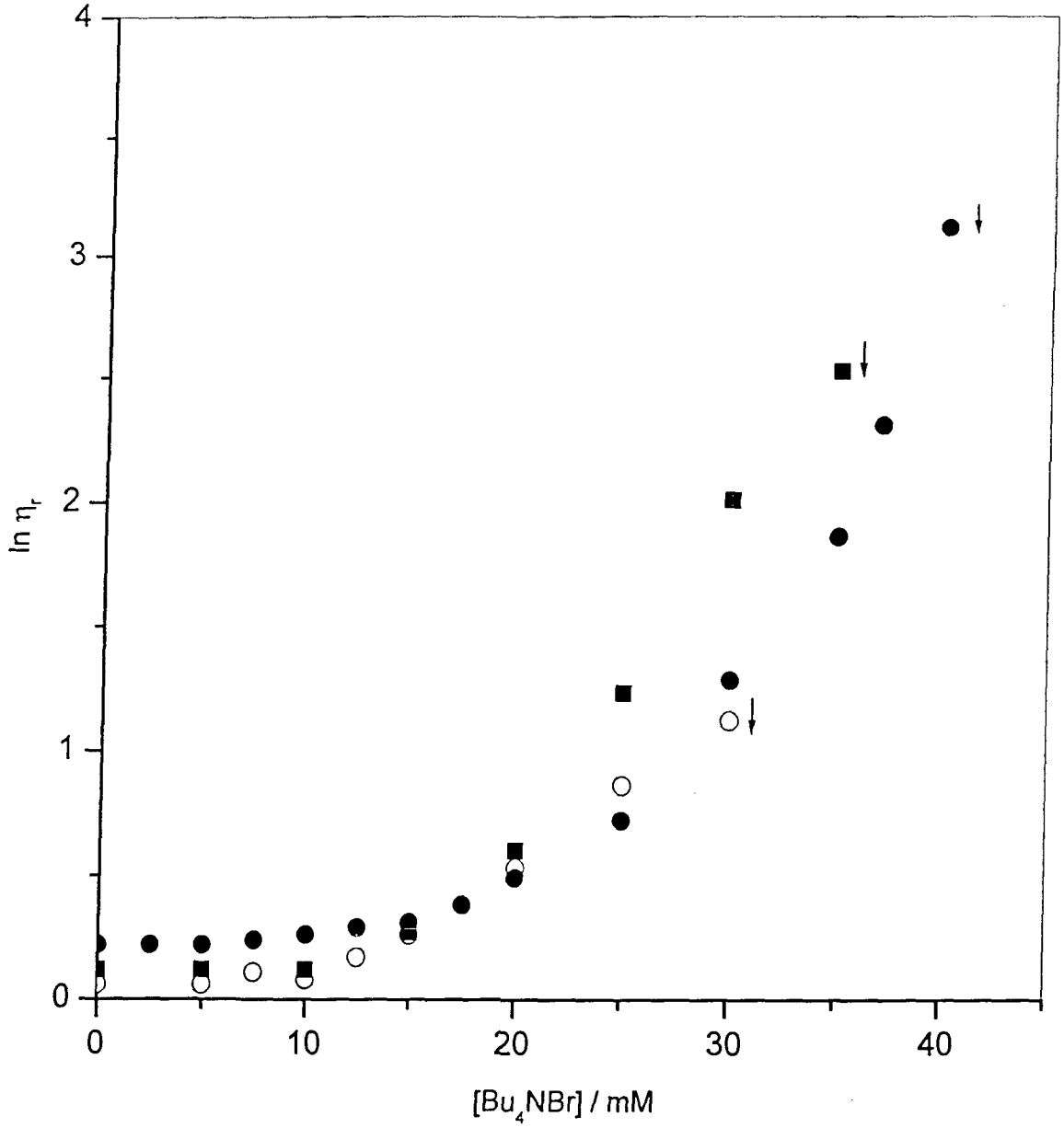

Fig. 5.2. Plots of relative viscosities (η_r) of x mM SDBS micellar solutions as a function of added Bu_4NBr (upto the solubility limits indicated by arrows) at 30 °C : x = 25, (○), 50, (■); 100 mM, (●).

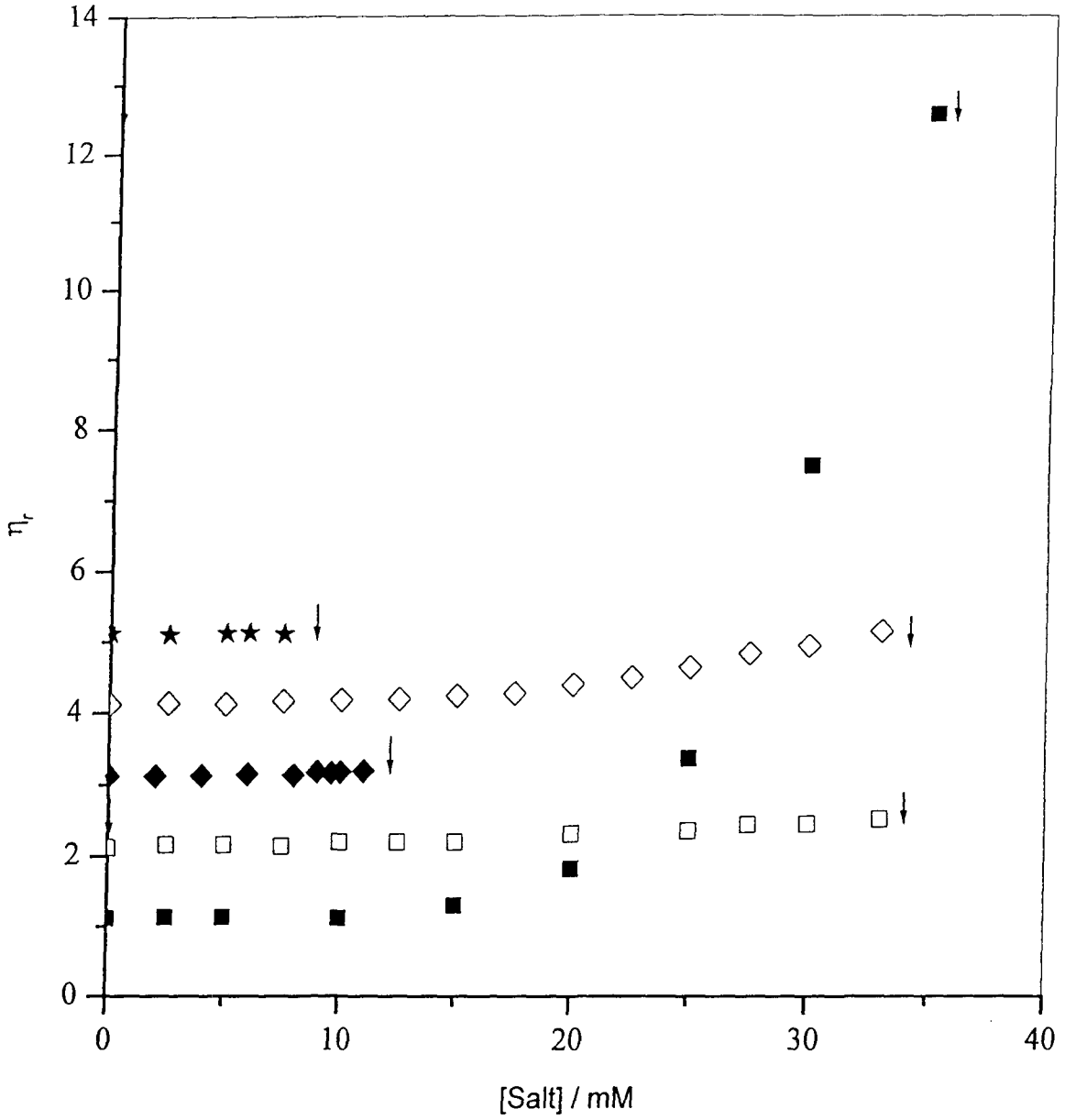

Fig. 5.3. Plots of relative viscosities (η_r) of 50 mM SDBS micellar solutions as a function of added quaternary salts (upto the solubility limits indicated by arrows) at 30 °C : (■), Bu_4NBr; (□), ϕ_4PBr; (◆), Bu_4PBr; (◇), $Pr\phi_3PBr$; (★), Am_4NBr. Plots are shifted vertically by 0, 1, 2, 3 and 4 units respectively, for clarity of presentation.

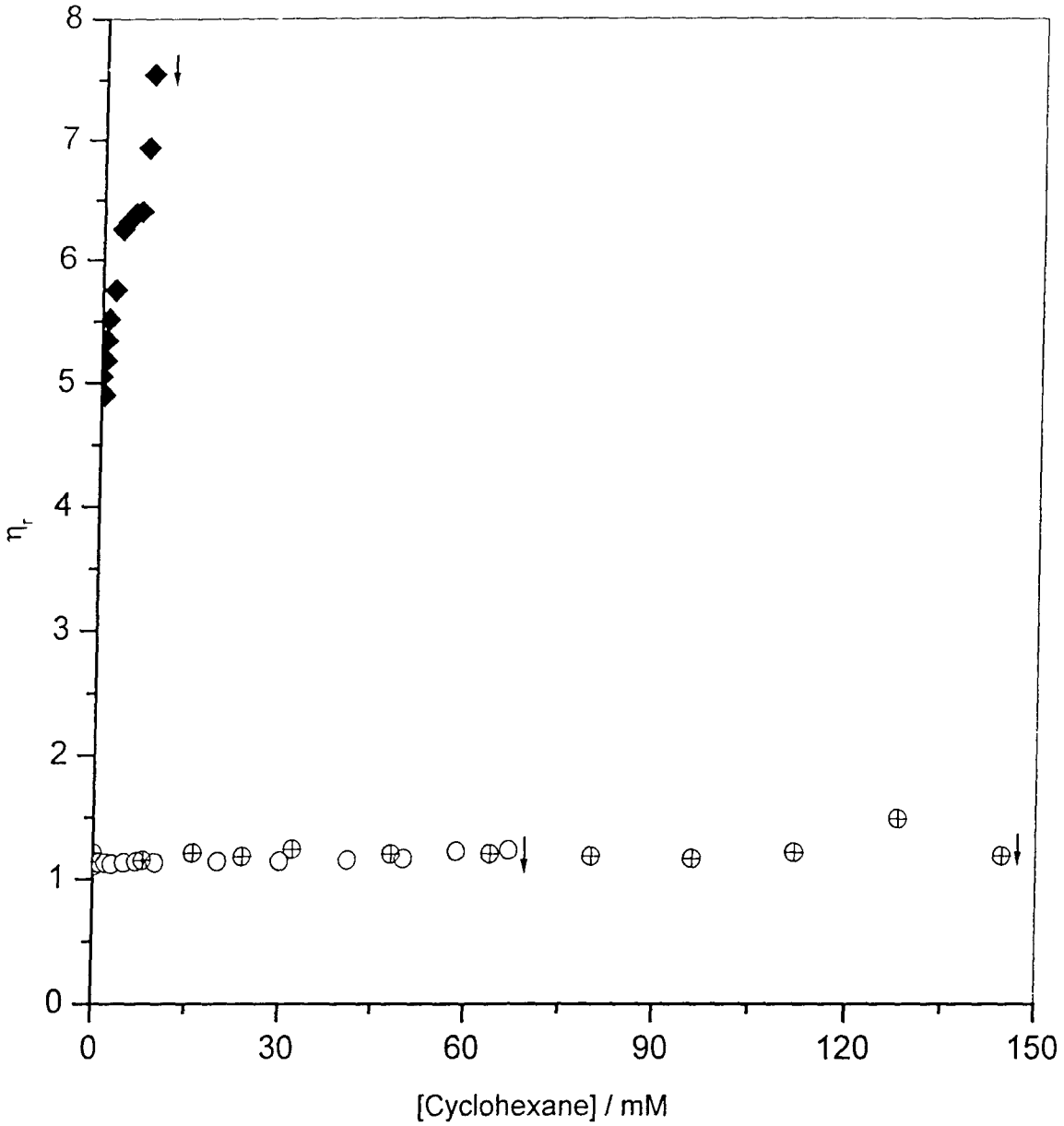

Fig. 5.4. Plots of relative viscosities (η_r) of 50 mM SDBS + x mM Bu_4NBr micellar solutions as a function of added cyclohexane (upto the solubility limits indicated by arrows) at 30 °C : x = 0.0, (○); 15, (⊕); 30 mM, (◆).

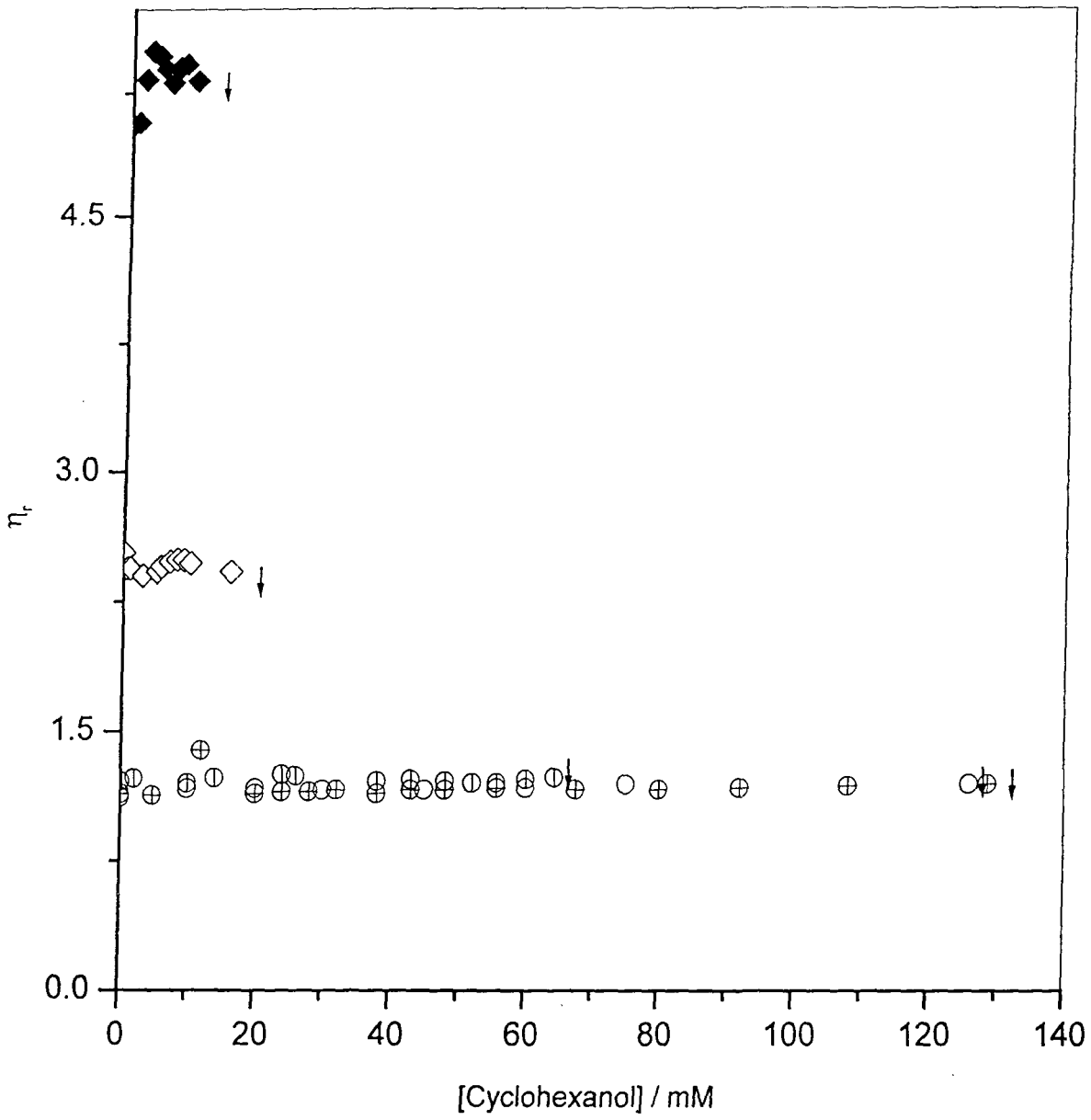

Fig. 5.5. Plots of relative viscosities (η_r) of 50 mM SDBS + x mM Bu_4NBr micellar solutions as a function of added cyclohexanol (upto the solubility limits indicated by arrows) at 30 °C : x = 0.0, (○); 10, (⊕); 15, (⊙); 25, (◇); 30 mM, (◆).

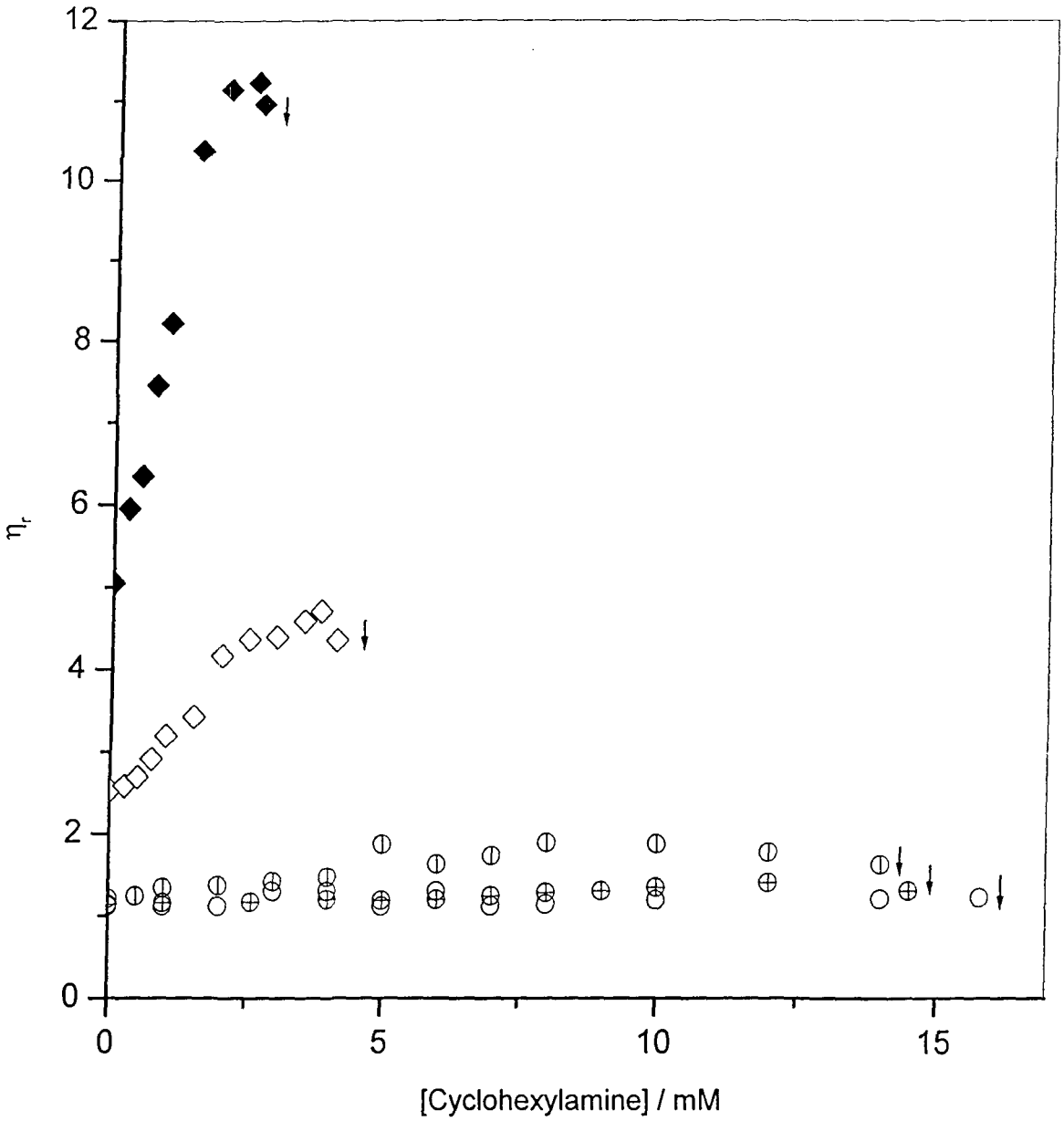

Fig. 5.6. Plots of relative viscosities (η_r) of 50 mM SDBS + x mM Bu_4NBr micellar solutions as a function of added cyclohexylamine (upto the solubility limits indicated by arrows) at 30 °C : x = 0.0, (○); 10, (⊕); 15, (◐); 25, (◇); 30 mM, (◆).

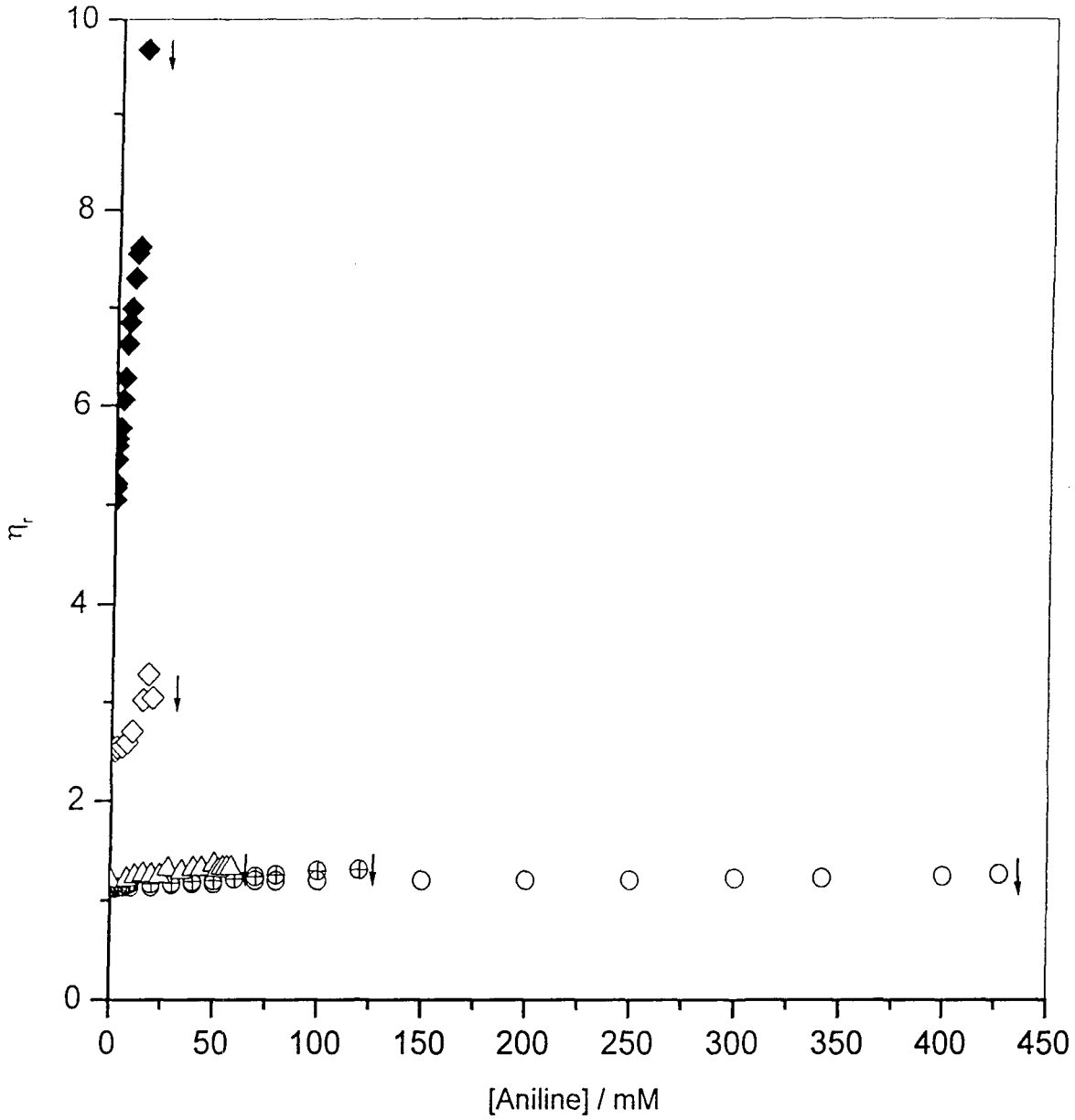

Fig. 5.7. Plots of relative viscosities (η_r) of 50 mM SDBS + x mM Bu_4NBr micellar solutions as a function of added aniline (upto the solubility limits indicated by arrows) at 30 °C : x = 0.0, (○); 10, (⊕) ; 15, (△) ; 25, (◇) ; 30 mM, (◆).

at a comparatively low concentration of Bu_4NBr (≈20 mM) which shows that Bu_4NBr is more effective to initiate micellar growth in SDBS solutions. The micellar growth takes place because Bu_4N^+ (produced in solution) possesses a large hydrophobic volume and hence interacts electrostatically as well as hydrophobically with SDBS micelle in the solution. The interaction of Bu_4N^+ would not affect the *l* of SDBS monomer in the micelle but the volume of micellar core may increase substantially due to intercalation of some butyl chains between monomers of the micelle. Therefore, the micellar volume increase is equivalent to increasing the effective volume of the monomer (*v*).[22] The positive charge of the Bu_4N^+ will decrease the effective a_h. Therefore, Bu_4N^+ can increase the surfactant packing parameter (R_p).[6]

Figure 5.3 shows the variation in η_r of 50 mM SDBS solutions with the addition of five different quaternary bromides. No significant changes in η_r are observed except with Bu_4NBr addition. It should be mentioned here that phenyl salts (ϕ_4 PBr and $Pr\phi_3PBr$) can provide more than one benzene ring to their respective counterions (ϕ_4P^+ or $Pr\phi_3P^+$). It is known that the π–electron cloud of the phenyl ring can interact in an opposite fashion with anionic surfactant to that with a cationic one.[23] Dodecylbenzenesulfonate (DBS^-) also has one benzene ring, and therefore, the system would have less hydrophobic interactions and less effect on η_r. This indeed is observed with the above salts. On the other hand, Bu_4PBr and Am_4NBr destabilized the system at fairly low concentrations which precluded studies of these salts at higher concentrations. R_4NBr salts have higher solubility and show rich viscosity pattern with SDS which may be due to higher SDS concentration

used in the systems and the difference in chemical structure of the two surfactants (SDS and SDBS).[24] On the basis of this study we chose a system containing 50 mM SDBS + Bu_4NBr to study addition of cyclohexane, cyclohexanol and cyclohexylamine.

Figure 5.4 illustrates the interplay between the effect of Bu_4NBr and cyclohexane concentration on the variation of η_r of 50 mM SDBS micellar solutions. The viscositiy remained almost constant when cyclohexane was gradually added in the absence or at 15 mM Bu_4NBr but a sharp change in η_r was observed at 30 mM Bu_4NBr. The constancy in η_r is due to the solubilization of cyclohexane in the interior of the micelle[25] whereas the change indicates formation of non-spherical micelles. This is due to the fact that as [Bu_4NBr] increases, the Bu_4N^+ causes increased counterion binding together with increased hydrophobic interactions. This combined effect would be responsible for a less hydrated headgroup region of SDBS micelle.[26] Further, the presence of Bu_4N^+in the headgroup region of the micelle would create its own hydrophobic region[17] where cyclohexane can now partition. The solubilization of the organic additive near to the headgroup region is the prime cause of micellar growth and increase of viscosity of the solution. This is indeed the case for the addition of cyclohexane to the 50 mM SDBS + 30 mM Bu_4NBr solution. It has been suggested that the size of the additive molecule (i.e., its molar volume), its polarity, its location in the aggregates, and its concentration influence the solubilization capacity of micelles;[27,28] thus, all the above factors, in turn, would determine the additive capacity to change micellar shape and/or size.

Figures 5.5 and 5.6 show the variation of η_r on addition of cyclohexanol and cyclohexylamine to 50 mM SDBS solutions containing different fixed concentrations of Bu_4NBr (0, 10, 15, 25 and 30 mM). With cyclohexanol, the viscosity behavior upto 25 mM Bu_4NBr is found to be the same as in case of cyclohexane (at lower salt concentrations). Similar is the case with cyclohexylamine addition in solutions containing [Bu_4NBr] $\leq$ 10 mM. With 15 mM of Bu_4NBr, the η_r shows a slight increase with the addition of cyclohexylamine while a more prominent increase in η_r is observed at [Bu_4NBr] = 25 mM. At 30 mM salt concentration, a distinct rise in η_r, a peak, and then a decrease has been observed with the continuous addition of both the additives. The behavior is understable by considering the following fact. Micelles have a number of solubilization sites as one moves toward the core from the bulk aqueous phase. When no Bu_4NBr is present in the system, both organic additives (cyclohexanol and cyclohexylamine), owing to their solubility characteristics,[29] would prefer to go inside the micelles and have practically no effect on η_r of the system. A similar effect was observed for other hydrocarbons with a cationic surfactant.[30] When sufficient amount (e.g., 30 mM Bu_4NBr) of the salt is present in the system, Bu_4N^+ counterions interact with anionic SDBS micelles. As stated earlier, four alkyl chains of the Bu_4N^+ would also prefer to go in the micellar headgroup region. This situation would produce polarity decrease of the headgroup region and would favor for organic additive solubilization in the region. The increased solubilization of these additives in the headgroup region would produce micellar growth and increase in the viscosity. This is indeed observed in Figs. 5.5 and 5.6.

At higher [organic additive] the viscosity decrease may be due to the fact that once the solubilization sites become saturated in the micellar palisade layer, these additives start going deep inside the core (rather than remaining in the vicinity of the interfacial region) and thus relaxing the requirement of surfactant chains to reach the center of the micelles.[24]

Further, solubilized molecules once inside the core, may increase the size of hydrophobic center and give swollen micelles (instead of grown micelles). Swollen micelles are supposed to be less viscous than the grown ones and form the basis of viscosity decrease. This indeed is observed with cyclohexanol and cyclohexylamine.

Figure 5.7 shows η_r–[aniline] plots for 50 mM SDBS micellar solutions containing lower as well as higher Bu_4NBr concentrations. Though the behavior is similar to that of cyclohexylamine, no peak was observed in this case upto the solubility limit. This may be due to the fact that [aniline] is not sufficient to produce core solubilization and hence no swollen micelles. The results of the present study allow to propose that the traditional micellar solubilization sites for an organic compound can be changed by appropriate selection of components (e.g., quaternary salts).

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CHAPTER VI

SANS STUDIES ON SODIUM DODECYLBENZENESULFONATE – TETRA-*n*-BUTYLAMMONIUM BROMIDE SYSTEMS

INTRODUCTION

The observation of partial miscibility in binary surfactants/water micellar solutions is commonplace.[1-7] There are frequent reports of both lower and upper consolute curves for nonionic and zwitterionic surfactants.[1,2] There even exists a few reports of lower consolute curves for ionic surfactants in water.[3, 8-10]

The phase boundary curve of miscibility gap is commonly known as the 'cloud curve'[11] in view of the pronounced turbidity of the solutions close to the phase separation. In the early days this clouding was ascribed to an increase in size and aggregation number [12,13] of the micelles and the formation of giant micelles which were believed to become eventually insoluble in water.[14] Later it was realized that the clouding results from the clustering of micelles due to the attractive intermicellar interactions and the term 'coacervate curve' was coined for concentrated micellar solutions with a conjectured liquid like packing of the micelles.[15-17] In the last two decades considerable attention has been paid to the scattering behavior[18-20] close to the critical point of these solutions. Hayter and Zulauf [19] have concluded from SANS experiments that the observed increase in the forward scattering is due to the formation of larger particles consisting of spherical micelles of fixed size. Strey and Pakusch[21] have suggested that the region of the isotropic solution (below LCB) may be divided into three sections: a region of single spherical micelles at low surfactant concentrations and low temperatures, aggregates of micelles in an intermediate range at higher mass fractions of the surfactant and higher temperatures and the critical region which is dominated by critical point fluctuations. This picture is widely

accepted for below LCB region although presently there is little knowledge about the structures near LCB. In a recent SANS study,[22] it was observed that micellar growth takes place as the system approaches the CP.

Recently, interest has focussed on the possibility that upper or lower critical points could occur within clear regions above or below the consolute boundaries. An upper consolute loop within a lamellar phase has been reported for binary anionic and cationic surfactants in water. However, lower and upper consolute loops are much rarer in the same system. Here, sections of lower and upper consolute boundaries have been produced by performing temperature variation effect on the visual appearance of solutions. For the purpose, SDBS was used as the surfactant and tetra-*n*-butylammonium bromide (Bu_4NBr) as the salt. SANS studies were performed in the clear region above the UCB and below the LCB. For the SANS measurements samples were prepared in D_2O. SANS data from 100 mM SDS were also collected for comparison purposes.

RESULTS

Figures 6.1 and 6.2 show the temperature–[Bu_4NBr] phase diagrams at different concentrations of SDBS. SANS spectra for surfactants SDS and SDBS at 30 °C are shown in Fig. 6.3 and the effect of Bu_4NBr on the SANS spectra of 100 mM SDBS at 30 °C is shown in Fig. 6.4. Effect of temperature on the spectra of 100 mM SDBS in presence of different fixed concentrations of Bu_4NBr are given in Figs. 6.5-6.7. SANS spectra for the effect of temperature on 50 mM SDBS + 32 mM Bu_4NBr are depicted in Fig. 6.8. The analyzed SANS parameters (N; fractional charge, α; semi-major

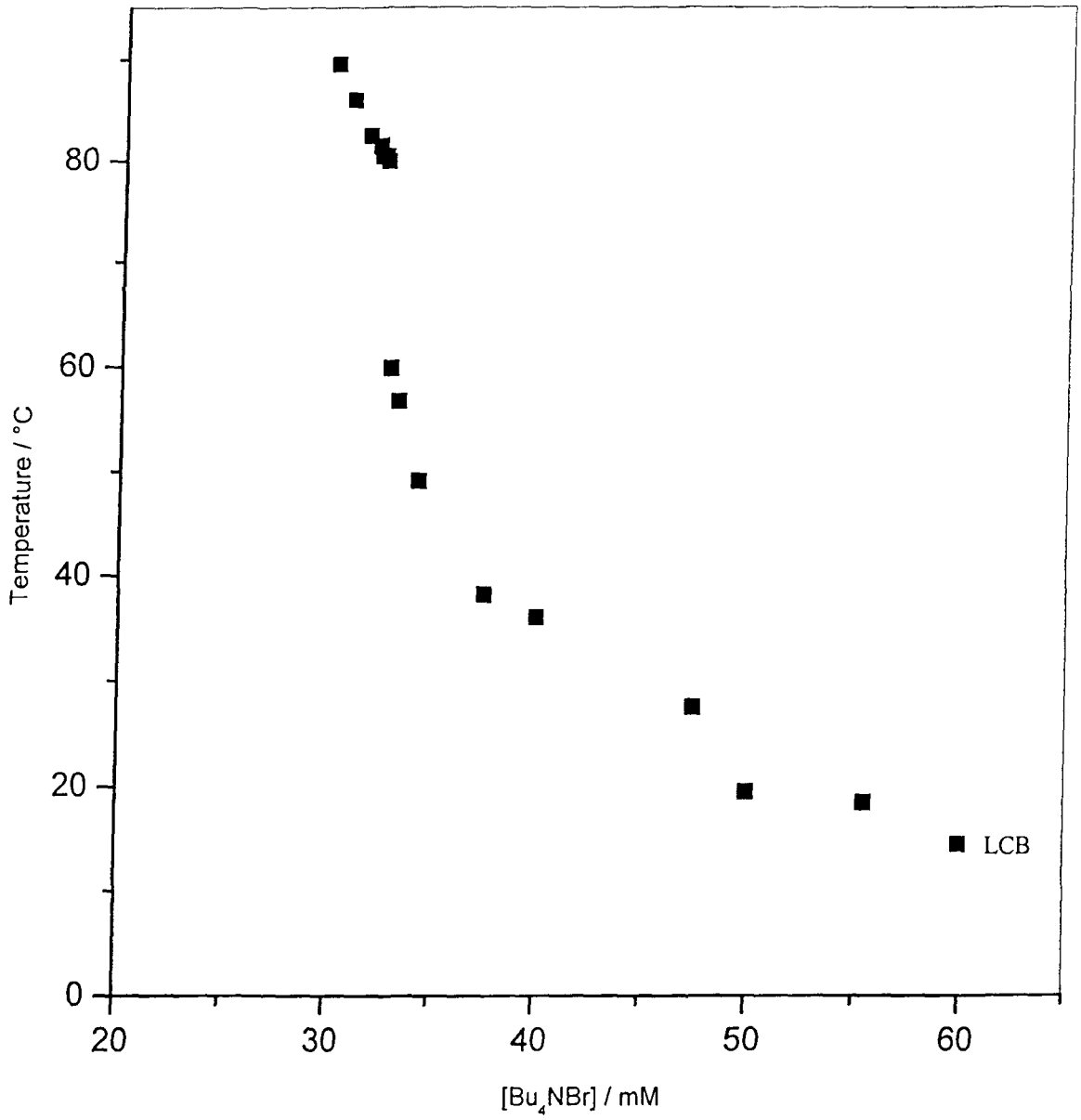


Fig.6.1. Temperature–[Bu_4NBr] phase diagram for the 50 mM SDBS–Bu_4NBr system. The curve represents the lower consolute boundary (■, LCB).

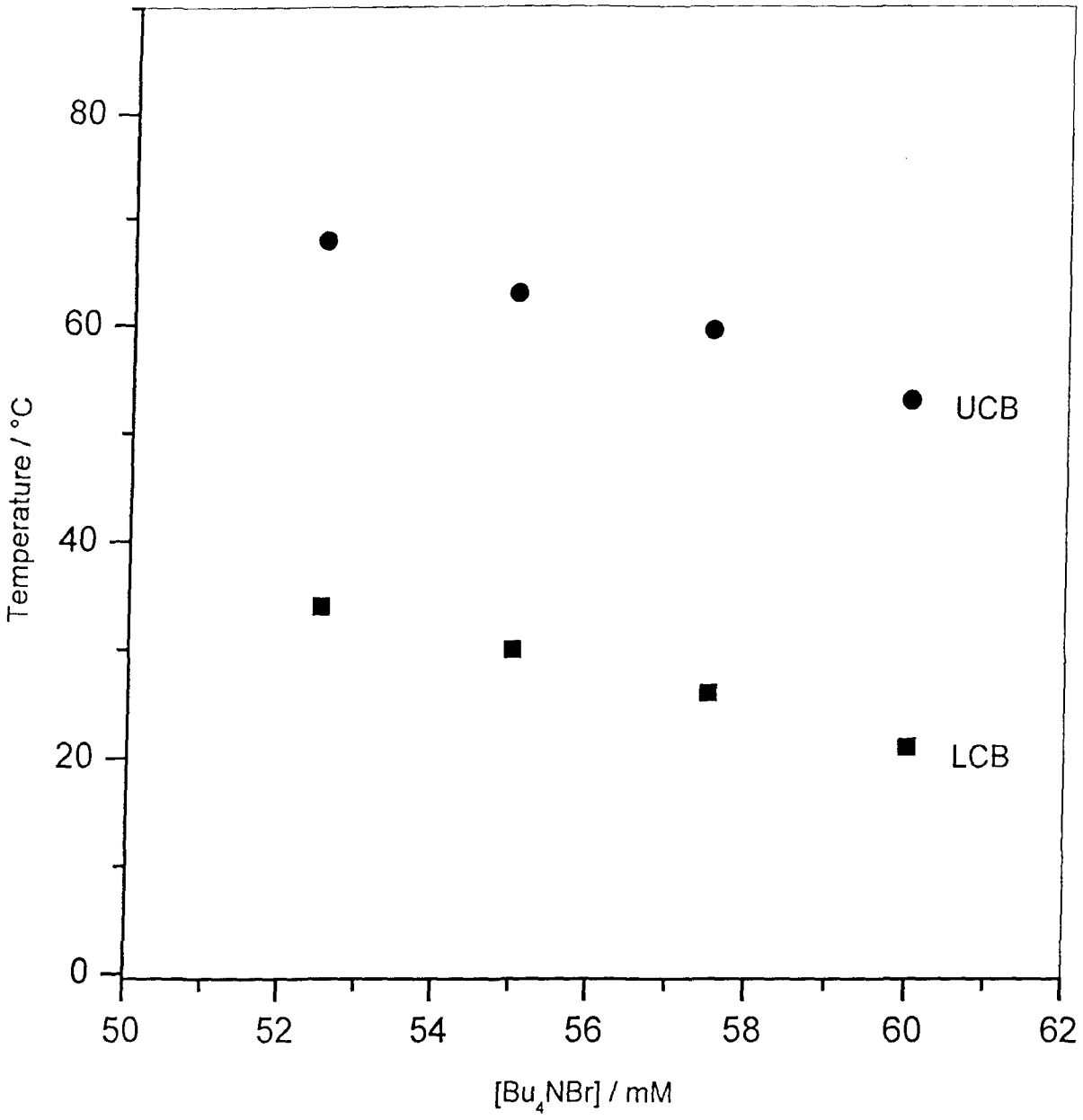


Fig.6.2. Temperature–[Bu_4NBr] phase diagram for the 100 mM SDBS–Bu_4NBr. system. The two sections of curves belong to lower consolute boundary (■, LCB) and upper consolute boundary (●, UCB).

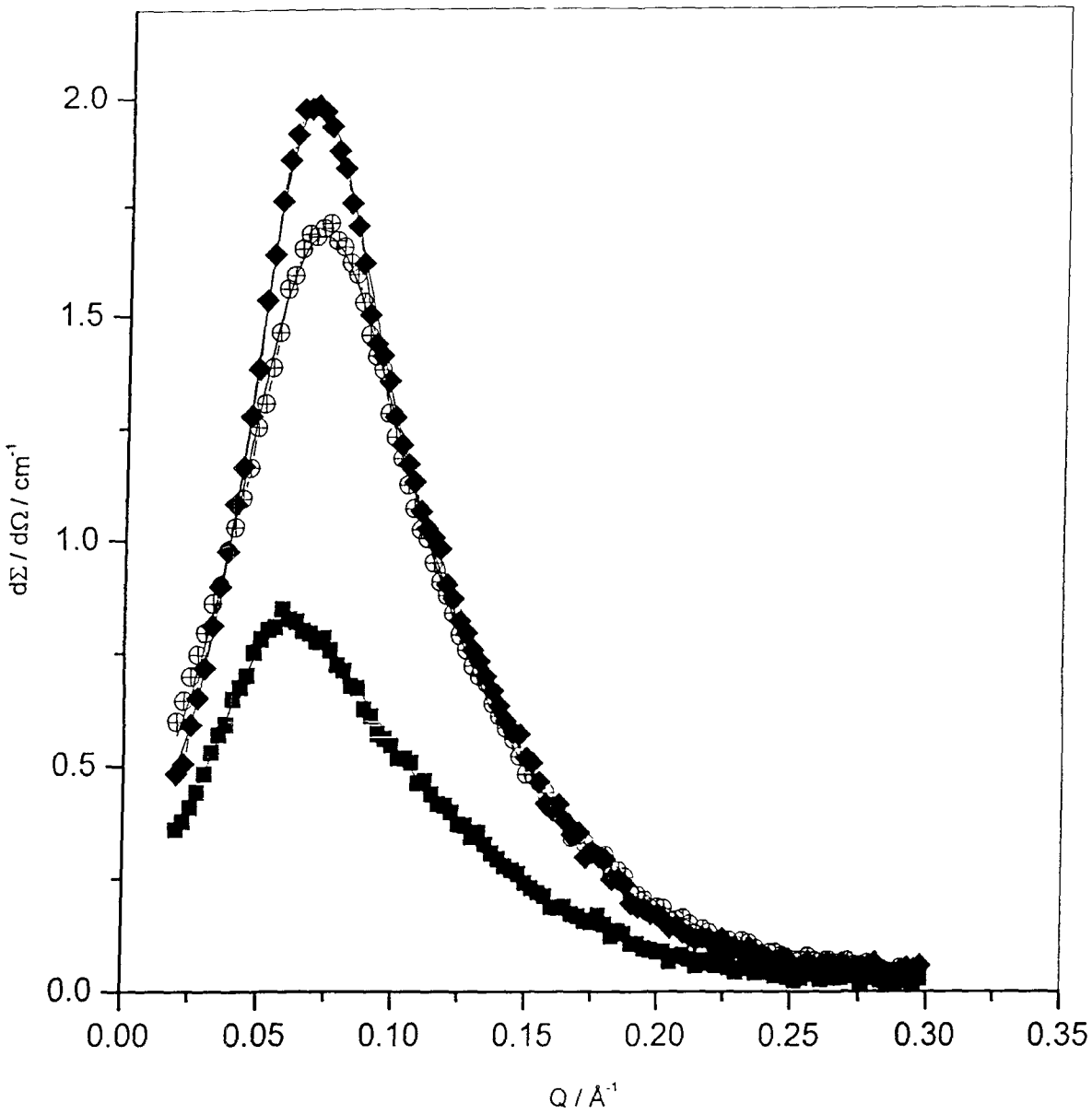


Fig.6.3. SANS spectra from different surfactant (SDS and SDBS) solutions at 30 °C : (■) , 50 mM SDBS; (⊕), 100 mM SDBS; (◇), 100 mM SDS. Solid lines are theoretical fits based on Hayter and Penfold-type analysis.

TABLE-6.1.

Micellar parameters for x mM surfactant obtained from Hayter-Penfold - type analysis at 30 °C.

x / mM	N	α	*c* /Å	*a=b* /Å	*c/a*	χ_r^2
100 (SDS)	72	0.24	25.9	15.2	1.70	0.04
100 (SDBS)	51	0.17	34.1	13.3	2.56	0.03
50 (SDBS)	44	0.18	30.6	13.1	2.33	0.01

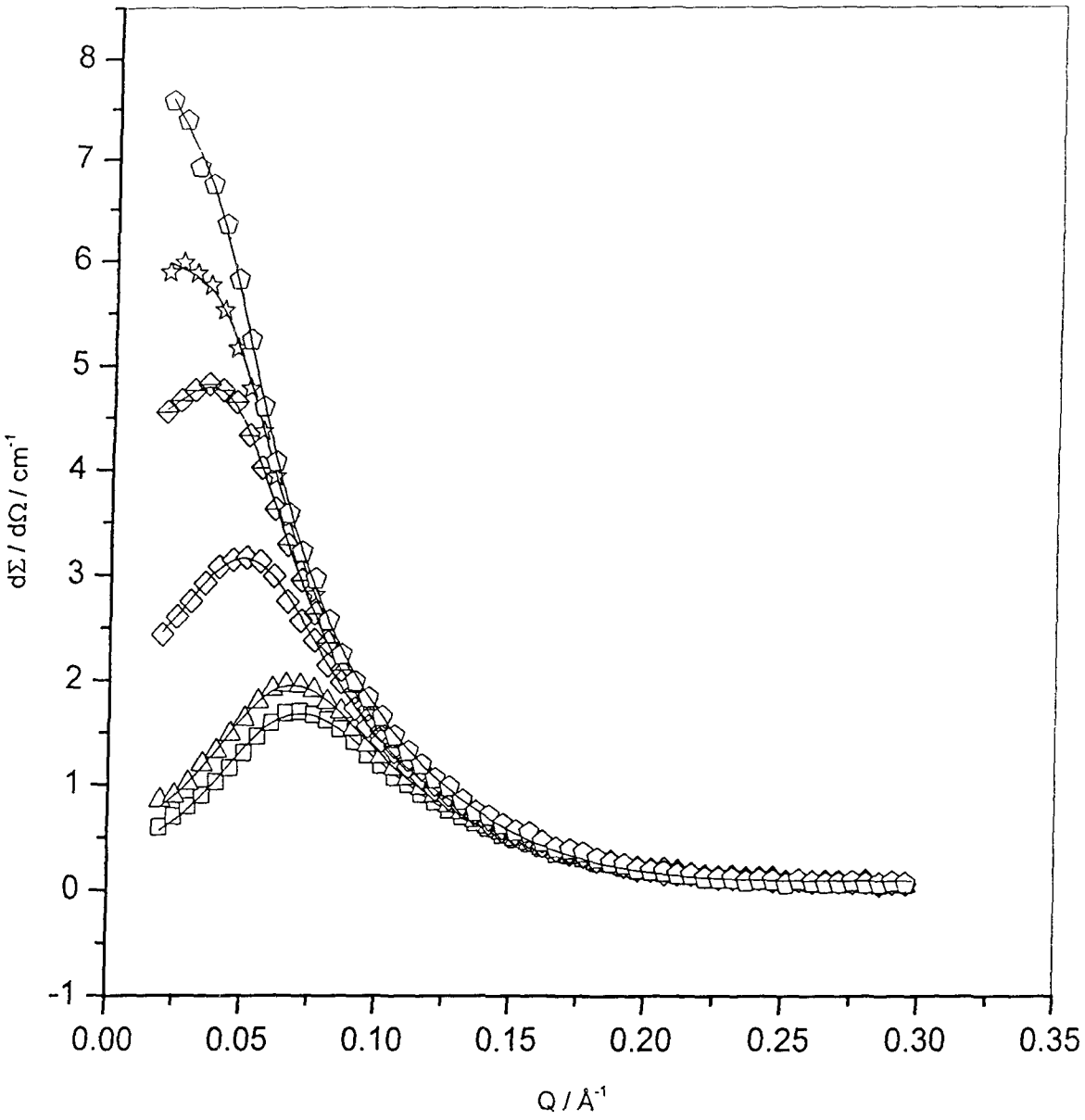


Fig.6.4. SANS spectra from 100 mM SDBS solutions with increasing concentrations (x) of Bu_4NBr at 30 °C : x = 0.0, (□); 5, (△); 15, (◇); 25, (◈); 32, (☆); 39.5 mM, (○). Solid lines are theoretical fits.

TABLE-6.2.

Micellar parameters for 100 mM SDBS + x mM Bu_4NBr obtained from Hayter-Penfold - type analysis at 30 °C.

x / mM	N	α	*c* / Å	*a=b* / Å	*c/a*	χ_r^2
0	51	0.17	34.1	13.3	2.56	0.03
5	58	0.17	37.8	13.7	2.76	0.03
15	105	0.10	62.2	14.7	4.23	0.04
25	192	0.10	109.2	15.4	7.09	0.06
32	228	0.09	126.8	15.9	7.97	0.06
39.5	300	0.09	162.6	16.4	9.91	0.22

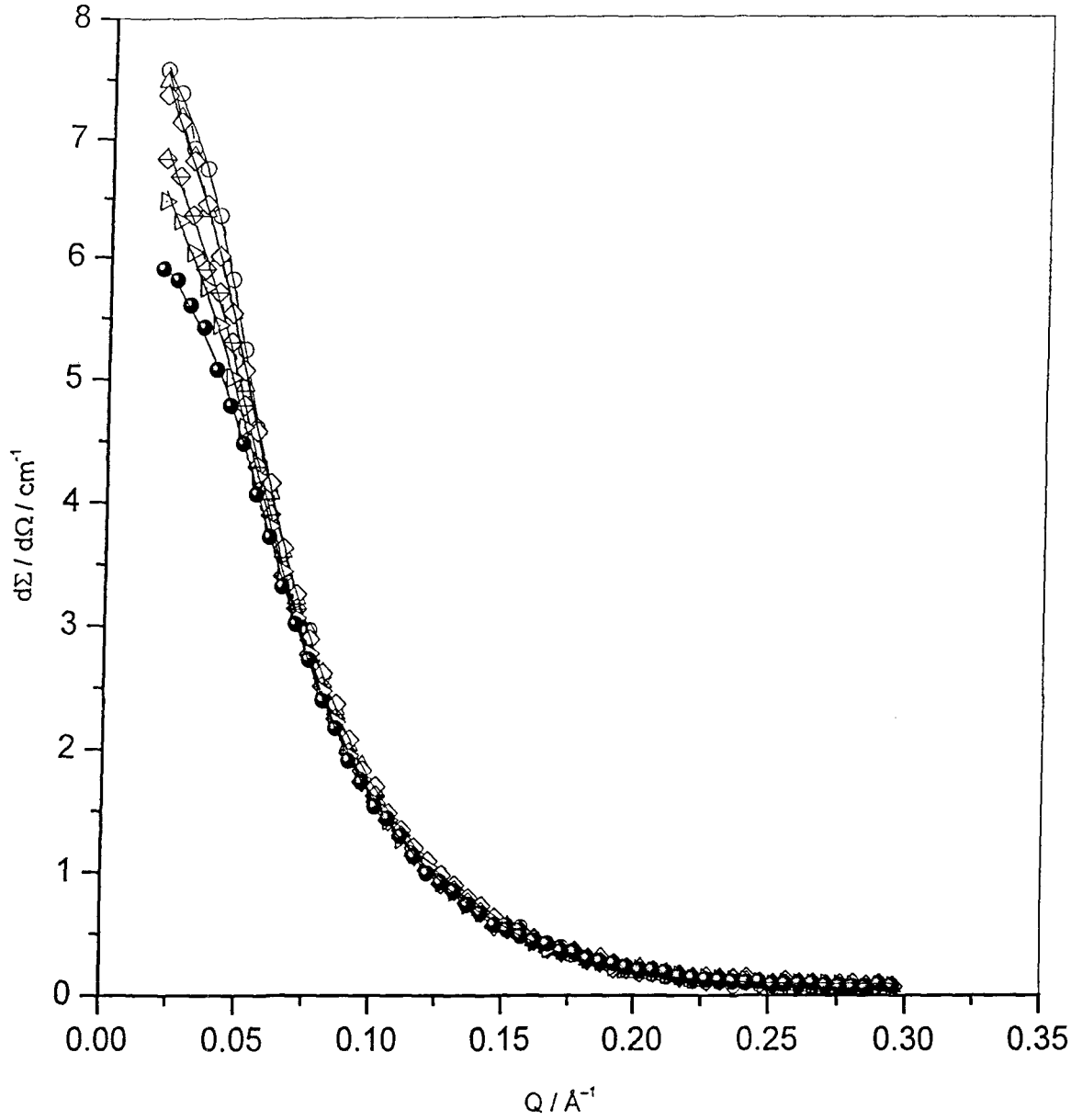


Fig.6.5. SANS spectra from 100 mM SDBS + 39.5 mM Bu_4NBr system at different temperatures : 30 °C, (○); 40 °C, (△); 50 °C, (◇); 60 °C, (◈);70 °C, (▷); 80 °C, (●). Solid lines are theoretical fits.

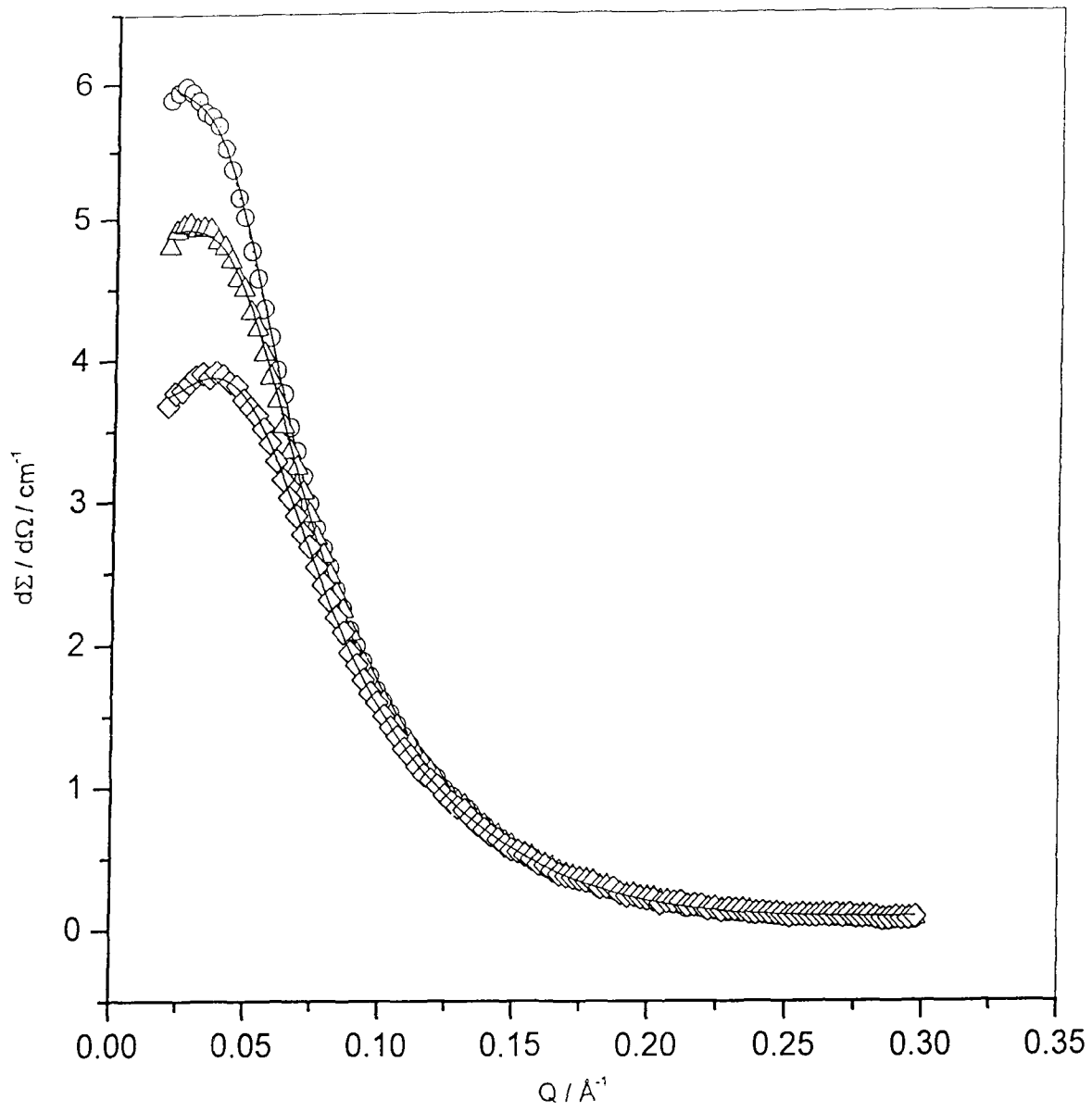


Fig.6.6. SANS spectra from 100 mM SDBS + 32 mM Bu_4NBr system at different temperatures : 30 °C, (○); 60 °C, (△); 80 °C, (◇). Solid lines are theoretical fits.

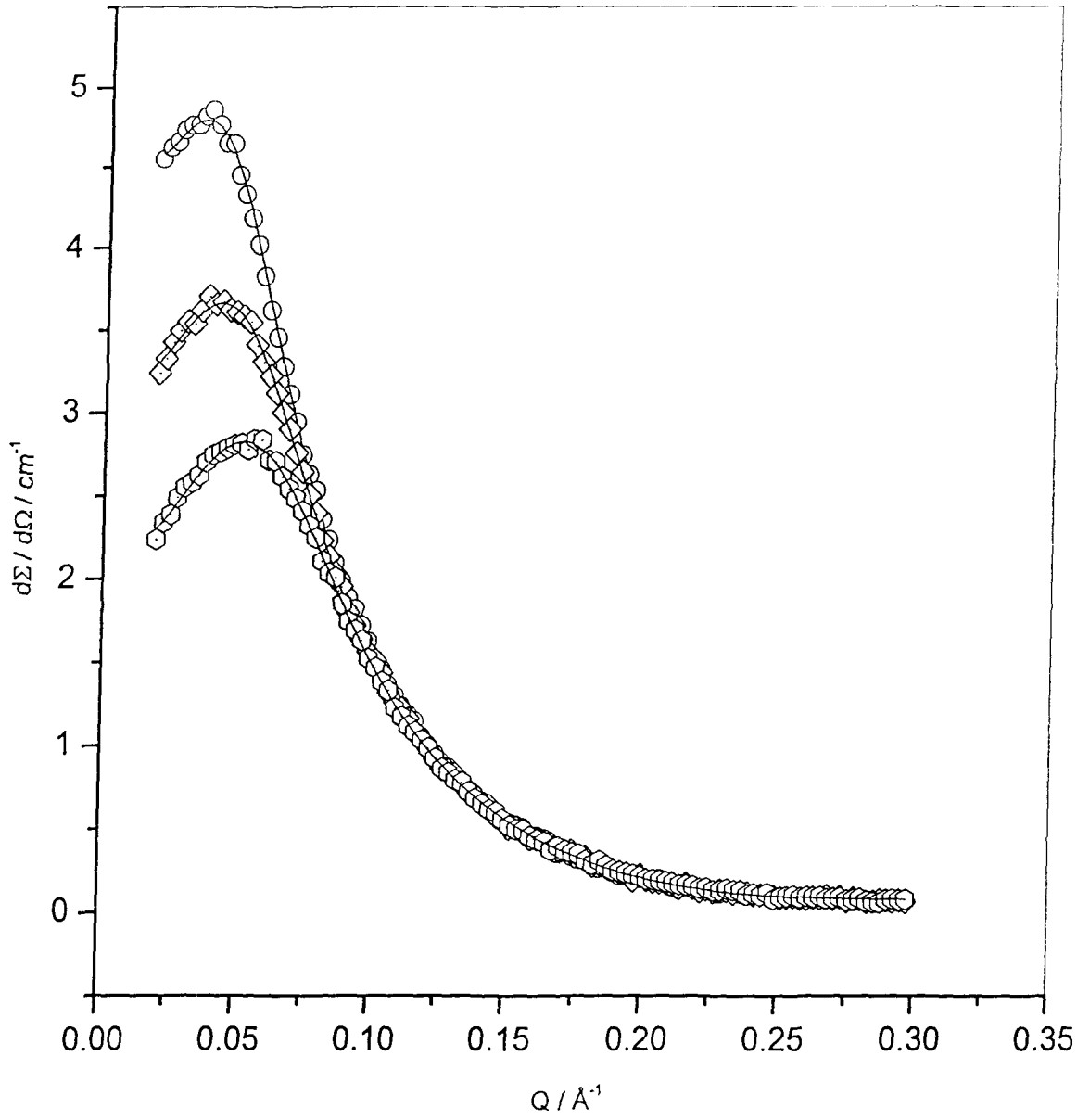


Fig.6.7. SANS spectra from 100 mM SDBS + 25 mM Bu_4NBr system at different temperatures : 30 °C, (○); 60 °C, (◇); 80 °C, (⊙). Solid lines are theoretical fits.

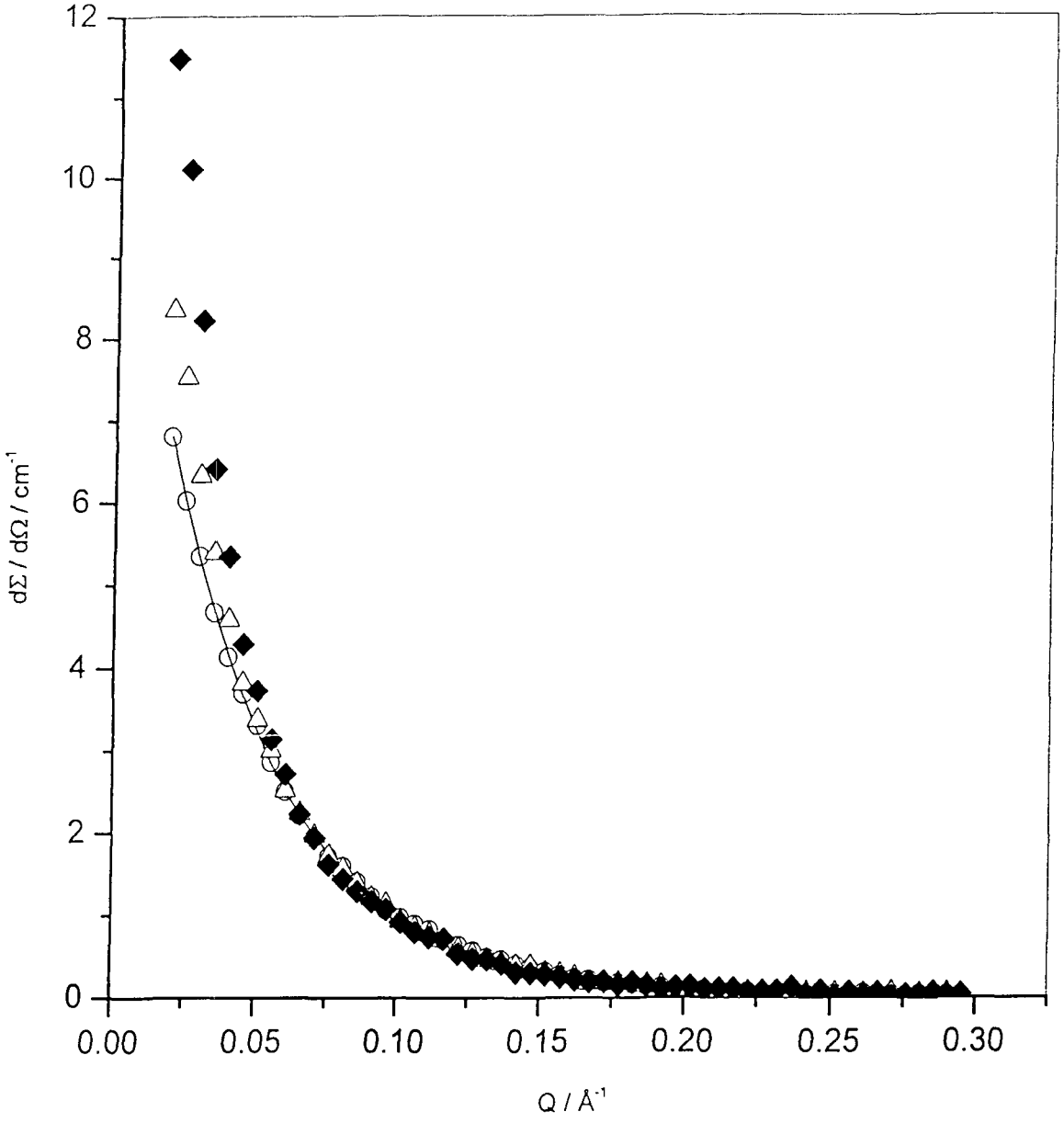


Fig.6.8. SANS spectra from 50 mM SDBS + 32 mM Bu_4NBr system at different temperatures : 30 °C, (○); 40 °C, (△); 50 °C, (◆). Solid line is theoretical fit.

TABLE-6.3.

Micellar parameters for 100 mM SDBS + 39.5 mM Bu_4NBr obtained from Hayter-Penfold - type analysis at different temperatures.

Temperature / °C	N	α	*c* / Å	*a=b* / Å	*c/a*	χ_r^2
30	300	0.09	162.6	16.4	9.91	0.22
40	258	0.09	144.6	16.1	8.98	0.14
50	253	0.07	140.1	16.2	8.65	0.13
60	239	0.07	133.7	16.0	8.36	0.21
70	219	0.07	124.7	16.0	7.79	0.07
80	196	0.07	113.0	16.0	7.06	0.10

TABLE-6.4.

Micellar parameters for 100 mM SDBS + 32 mM Bu_4NBr obtained from Hayter-Penfold - type analysis at different temperatures.

Temperature / °C	N	α	*c* / Å	*a=b* / Å	*c/a*	χ_r^2
30	228	0.09	126.8	15.9	7.97	0.06
60	169	0.09	97.1	15.6	6.22	0.05
80	126	0.09	75.6	15.3	4.94	0.03
30*	298	0.06	166.7	16.91	9.86	0.07

* parameters of this row are for 50 mM SDBS + 32 mM Bu_4NBr belonging to below LCB region.

TABLE-6.5.

Micellar parameters for 100 mM SDBS + 25 mM Bu_4NBr obtained from Hayter-Penfold - type analysis at different temperatures.

Temperature / °C	N	α	*c* / Å	*a=b* / Å	*c/a*	χ_r^2
30	192	0.10	109.2	15.4	7.09	0.06
60	123	0.10	73.2	15.1	4.85	0.05
80	80	0.12	52.8	14.7	3.59	0.03

axis, *c* ; semi-minor axis, *a*) for various micellar systems are summarized in Tables 6.1-6.5.

Data treatment

The raw data were corrected for the background, empty cell scattering and sample transmission. The corrected intensities were normalized to absolute cross-section units and thus $d\Sigma/d\Omega$ *vs.* Q was obtained.[23] The experimental data points were fitted by adopting the routines as described by Hayter and Penfold,[24,25] and Chen and coworkers.[26,27] The data have not been corrected for resolution effects. Analysis of a limited set of data showed that resolution corrections do not alter the aggregation number of the micelle, especially when SANS data show a peak. The residuals in the fitting were negligible.

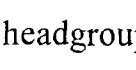
Data analysis

The relevant SANS theory is summarized as : for homogenous monodisperse micelles of volume V_P present at number density n_P and of coherent length density ρ_p, dispersed in a medium of scattering length density ρ_m, the coherent differential scattering cross-section ($d\Sigma/d\Omega$) is written as[24,25,28-30]

$$d\Sigma/d\Omega = n_p V_p^2 (\rho_P - \rho_m)^2 \; P(Q) \; S(Q) + B \qquad (6.1)$$

where P(Q) is the single (orientationally averaged) particle form factor which depends on the size and shape of the particle and S(Q) is the interparticle structure factor. B is a constant term that represents the incoherent scattering, which is mainly due to hydrogen atoms in the sample.

For the analysis, the micelles were assumed to be monodisperse, prolate ellipsoids, ($a=b\neq c$), where the sphere is a special case. It may be

mentioned, however, that elongated micelles usually tend to be of varying sizes and may not be monodispersed, but Eq. (6.1) is not valid for the polydisperse system. It was further assumed that the micelles have a hydrophobic core composed of dodecyl chains and a hydrated hydrophilic shell composed of headgroups (—  —SO_3^-), some fraction of Na^+, Bu_4N^+, and the solvent molecules (D_2O). Although we are aware of the limitations of such assumptions, it is not possible to get information on size distribution of micelles from the present data because of the involvement of too many unknown parameters in the data analysis. Thus, in the present analysis we have assumed the system to be monodisperse to avoid additional complexities.

The aggregation number (N) for the micelle is related to the V_P by the relation $n = V_P/v$, where v is the volume of surfactant monomer. P(Q) for anisotropic micelles (e.g., ellipsoidal) is given by

$$P(Q) = \int_0^1 [F(Q, \mu)]^2 \, d\mu \qquad (6.2)$$

The form factor $F(Q, \mu)$ is given by

$$F(Q,\mu) = 3 (\sin \omega - \omega \cos \omega) / \omega^3 \qquad (6.3)$$

where $\omega = Q [a^2\mu^2 + c^2 (1-\mu^2)]^{1/2}$ and μ is the cosine of the angle between the axis of revolution and Q. Therefore, P(Q) is dependent on both semi-minor (a) and semi-major (c) axes.

The volume of SDBS monomer was taken to be 498Å^3, as given by Tanford's formula.[31] S(Q) was calculated using standard methods.[29,30] This theory is applicable if there is no angular correlation between the micelles which is reasonable for charged micelles. It may be mentioned that a

satisfactory data analysis method for charged rod shaped micelles have not yet been developed. In this analysis the calculated spectra have three parameters, viz., the effective charge per monomer (α), *a*, and *c* or N.

SANS data were analyzed using the method discussed above and parameters α, *a*, *c* and N were computed. Solid lines in $d\Sigma/d\Omega$ vs. Q curves (Figs. 6.3-6.8) are the calculated fits.

DISCUSSION

The temperature – [Bu_4NBr] phase diagrams (Figs. 6.1 and 6.2) show that the nature of appearance of consolute boundaries are dependent upon [SDBS]. With 50 mM SDBS only LCB was obtained while with 100 mM SDBS both LCB and UCB were obtained by increasing the temperature and [Bu_4NBr]. Samples for SANS measurements were chosen from the clear regions above UCB and under LCB. Since SANS studies were performed with samples prepared in D_2O, the actual parameters would be different in the two types of solvent medium (H_2O or D_2O).

Before performing actual experiments, a few SANS spectra were obtained with SDBS solutions and compared with 100 mM SDS solution (Fig. 6.3). The perusal of micellar parameters in Table 6.1 indicates that *micelles are bigger in case of SDS than SDBS. SDBS molecule is longer* than SDS due to the presence of —⟨⟩— in the former, but $d\Sigma/d\Omega$ is higher in case of SDS (Fig. 6.3). The drop in N of SDBS may be due to the fact of a voluminous group being present in the headgroup region. As a result, the headgroups cannot come closer beyond a certain limit due to repulsive interactions of π-electron cloud of the benzene rings present in the monomers of the micelles. To alleviate these unfavorable electrostatic

consequences, the hydrocarbon chains in the micelles of SDBS take up folded conformations and hence SDBS micelles would experience relatively more wet environment than the SDS ones. In comparison, the hydrocarbon chains could be more extended in case of SDS and the terminal CH_3 group is burried significantly deep inside the micellar core. Hence *a* of SDS is expected to be more than of SDBS. The higher values of N and *a* confirm these propositions (Table 6.1). SANS spectra of 100 mM SDBS with added [Bu_4NBr] are given in Fig. 6.4. Each spectrum contains a well-defined interaction peak, characteristic of dispersions of charged particles, which disappears at 39.5 mM Bu_4NBr. This change is because of micellar growth and screening of the repulsive forces between the particles. The micellar growth is consistent with the viscosity and SANS results obtained for the same salt added to aqueous SDS.[32,33] The higher N and low α values are also consistent with the micellar growth in these systems with the addition of Bu_4NBr (Table 6.2).

On the basis of the above studies, the system 100 mM SDBS + 39.5 mM Bu_4NBr, which belongs to the clear region above UCB was chosen (the system remained turbid upto ~ 29 °C in D_2O). The SANS spectra of this system at different temperatures are given in Fig. 6.5. At 30 °C, the $d\Sigma/d\Omega$ diverges in the region of low Q (< 0.02 $Å^{-1}$). This type of behavior usually occurs with ionic micelles at higher salt concentrations[34] or with nonionic micelles at higher temperatures.[35] With a higher value of N and low value of α (Table 6.3), it can be safely assumed that the micelles in this system have some characteristics of nonionic surfactant systems. Interestingly, the increase of temperature (Fig. 6.5)

shows a decrease in $d\Sigma/d\Omega$ (in the low Q region) and, at 80 °C, an interaction peak starts reappearing. $d\Sigma/d\Omega$, however, remains independent of temperature in the region of large Q (> 0.10 $Å^{-1}$). To substantiate the temperature effect results further, SANS spectra were collected for lower concentrations of added Bu_4NBr (32 mM and 25 mM, Figs. 6.6 and 6.7, Tables 6.4 and 6.5). Lowering of $d\Sigma/d\Omega$ occured in these cases also with well defined interaction peaks from which we can infer that the micelle characteristics are changed from nonionic to ionic with the rise of temperature. This is also supported by the increased α values obtained at higher temperatures (Table 6.5). However, this behavior is opposite to the behavior reported for SDS + Bu_4NBr system where the α value decreased with increase in temperature. This may be due to the system's position in the phase diagram. The earlier reported system[22] seemingly belongs to under the LCB while the present ones belong to above UCB. This also shows that the position of a particular system in the phase diagram is important for the overall behavior.

The temperature effect on a system belonging to the region under LCB (50 mM SDBS + 32 mM Bu_4NBr, Fig. 6.8) is in sharp contrast with that observed with systems belonging to above UCB. Here, the temperature increase causes an increase in $d\Sigma/d\Omega$ at low Q while it is independent of the temperature in the large Q (> 0.075 $Å^{-1}$) region. The increase in $d\Sigma/d\Omega$ with temperature rise at lower Q is, in a sense, similar to that observed in nonionic micellar solutions where interactions are dominated by the Van der Waals forces.[35] Here, no interaction peak is observed with increase in temperature. Table 6.4 data for 30 °C show that, even with a low surfactant

concentration, significant increase in N has taken place. Seemingly, it is the effective salt concentration that plays a major role in deciding the final aggregate morphology. The availability of limited data in this region (below LCB) does not permit to make further comments.

Although the above studies are able to demonstrate successfully the different behavior of systems belonging to above UCB and below LCB regions, it should be pointed out that, in order to see any difference in phase regions for samples in H_2O and D_2O, precise CP measurements in D_2O should be made before making detailed morphological SANS studies.

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